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Titanium Assisted Alkylations of Selected Alkynols

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TITANIUM ASSISTED ALKYLATIONS OF SELECTED ALKYNOLS

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In Partial Fulfillment

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Master of Arts

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by

Leslie C. Smedley, Jr.

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APPROVAL SHEET

This thesis is submitted in partial fulfillment of the requirements for the degree of

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Approved, December 1976

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David W. Thompson

DEDICATION

This thesis is dedicated to Dr. Robert Orwoll, the first professor I can honestly consider as a true friend, and to Dr. Richard Stebbins, who believed in me even after I had made a wrong turn.

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ACKNOWLEDGEMENTS

The writer wishes to express his appreciation to Drs. David Thompson and Randolph Coleman under whose guidance this research was conducted, for their encouragement, support, and constructive criticism.

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ABSTRACT

The purpose of this research is to study the titanium assisted alkylations of a series of seven alkynols.

Initial addition of an alkynol to a solution of diethylaluminum chloride yields an ethyl(alkynoxy)aluminum chloride• diethylaluminum chloride adduct. Addition of the organoaluminum adduct to dichlorobis(pentahaptocyclopentadienyl)-titanium(IV) leads to a modified Zeigler catalyst system.

In the catalyst system, both the oxygen atom and the pi cloud of the alkynol are associated with coordination sites of the titanium. The pi cloud coordination facilitates the addition of an ethyl moiety across the triple bond; the stereochemistry of the hydrolysis product(s) appears to be dependent upon the initial substituents about the triple bond.

An intramolecular mechanism is suggested since 2-propyn-1-ol and 5-hexyn-1-ol do not react to give isolable amounts of ethylated product, and because no ethylated alkynol, or allene products are detected.

Optimized reaction conditions for the 3-butyn-1-ol ethylation involve reaction for 4 hrs at 0^{o} in methylene chloride, a 2.5:1 ratio of $AlEt_2Cl$:alkynol, and a 0.1:1 ratio of $TiCp_2Cl_2$:alkynol. Product yields of greater than 80% are reported.

Substantial yields of 4-pentyn-2-ol(66%), 4-pentyn-1-ol (74%), 4-phenyl-3-butyn-1-ol(43%), and 3-pentyn-1-ol(46%) ethylation products are reported utilizing the same reaction conditions except that the ratio of $TiCp_2Cl_2$:alkynol is increased to 0.5:1.

TITANIUM ASSISTED ALKYLATIONS OF SELECTED ALKYNOLS

CHAPTER I

INTRODUCTION AND GOALS OF RESEARCH PROJECT

Hydroalkylation addition reactions taking place at an isolated carbon-carbon triple bond are important as a means of producing substituted olefinic compounds. Hydroalkylation refers to the addition of an alkyl group to one carbon of the multiple bond, and the addition of a hydrogen atom to the other carbon. A generalized representation is shown in Figure 1.

The goal of the research described herein was to examine hydroalkylation reactions for the specific class of compounds designated alkynols. As shown in Figure 2, the generalized hydroalkylation of alkynols could yield a maximum of four possible products, two pairs of geometrical isomers. A stereospecific alkylation of alkynols which generates selectively substituted alkenols would be of considerable interest.

The approach to this study stems from an important area of interest in chemistry, the Zeigler-Natta catalyst systems for polymerization of olefinic and acetylenic compounds. Zeigler-Natta systems, which utilize transition metal (usually titanium) complexes and an alkylaluminum species, promote repeated metalloalkylations of unsaturated hydrocarbons, often in a stereospecific manner. These systems are used in forming linear and stereoregular polymers of high molecular weight.

A review of the Zeigler catalytic systems[1] as related to the polymerization of olefins suggests that a modification of them could be useful in hydroalkylating alkynols. While titanium has been established to be the active polymerization center, the aluminum alkyl species is important

Figure 1.

Generalized Hydroalkylation Reaction at
a Carbon-Carbon Triple Bond

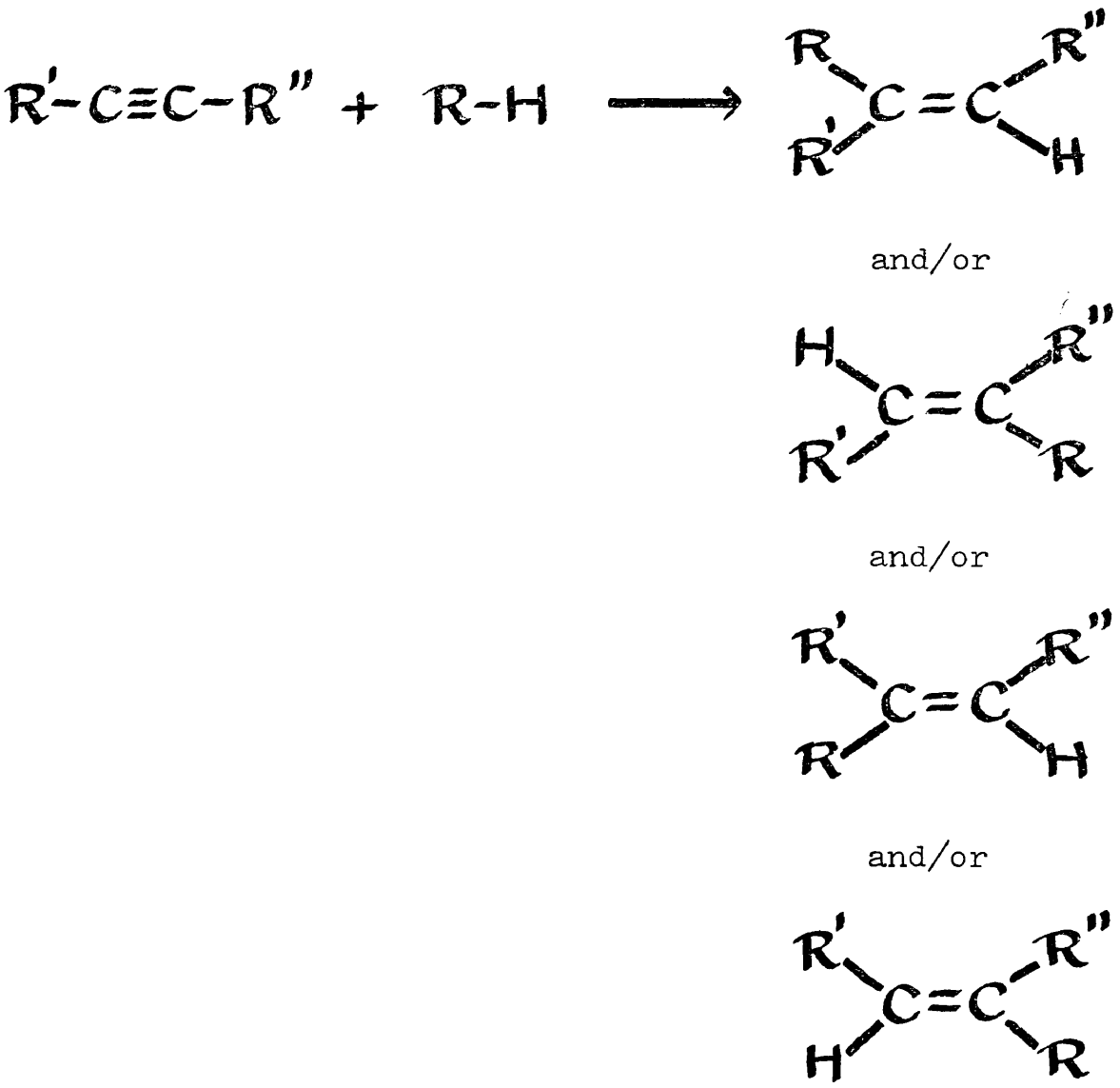
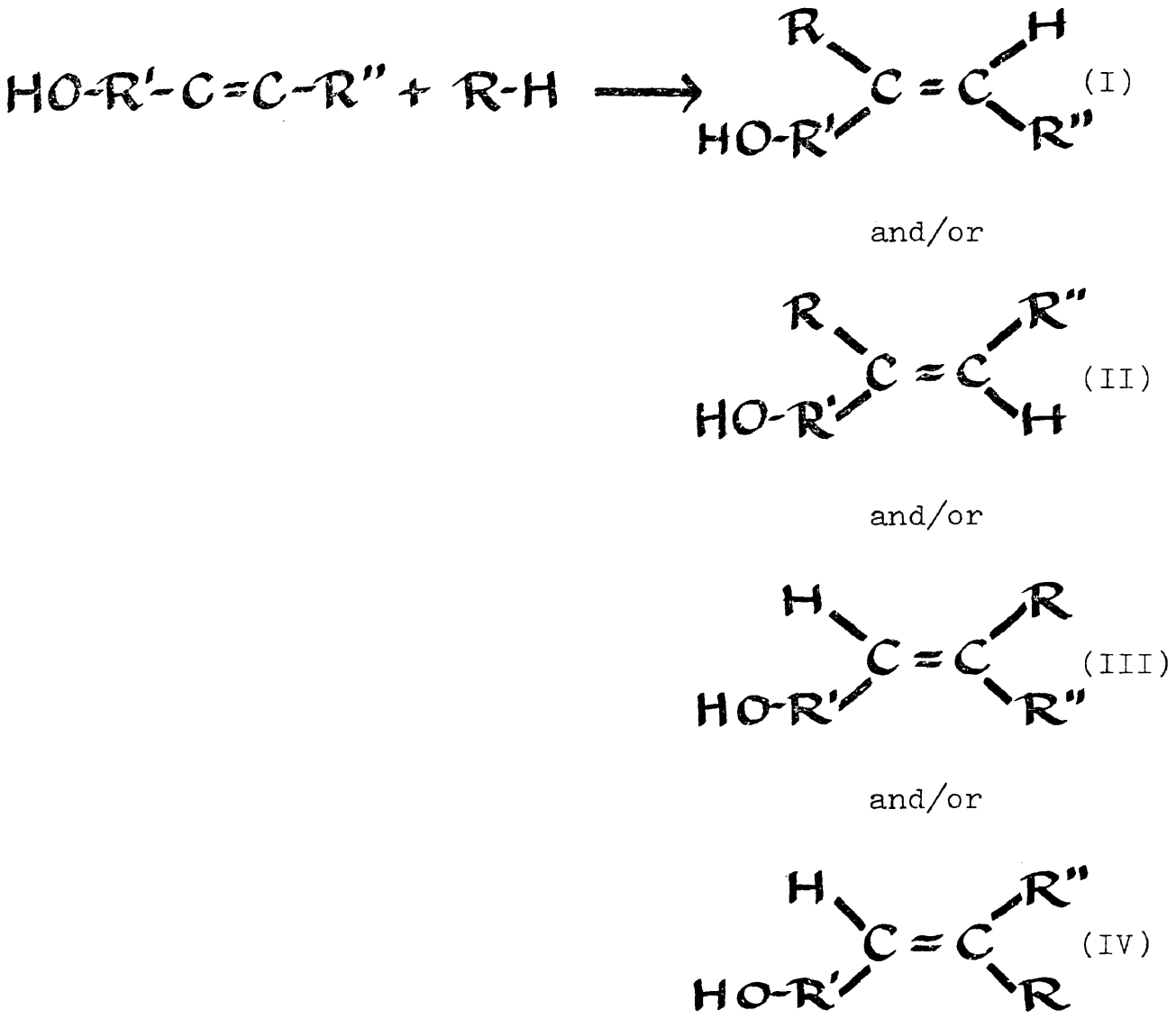


Figure 2.

Generalized Hydroalkylation of Alkynols



to the success of the system since it joins with the transition metal species through halide or alkoxide bridges and alkylates titanium via ligand exchange to form an active species. The titanium atom, which has a vacant site in its coordination sphere (assuming six is the preferred coordination number), then binds an olefinic monomer through the π cloud. As an electron from the ti-R bond is promoted to the molecular orbital of the complex, a four-centered transition state is formed. Collapse of the transition state brings about the insertion of the coordinated olefin into the ti-R linkage, forming a new titanium-alkyl linkage and regenerating the vacant titanium coordination site. The vacant site is occupied by another olefinic monomer, and the process is repeated.[2] The model used in Figure 3 depicts the polymerization of an olefin, although Zeigler catalytic systems have been used to polymerize alkynes as well.[3]

One adaptation of Zeigler catalyst systems to the specific goal of hydroalkylating alkynols is illustrated in Figure 4. Here a titanium-alkynoxy complex in the presence of an alkylaluminum undergoes intramolecular alkyne activation. This is followed by insertion of the triple bond into the alkyltitanium linkage. Assuming that hydrolysis occurs with retention of configuration, three possible hydrolysis products may be produced, depending upon the regioselectivity of the alkylation. For the alkylation occuring at the acetylenic carbon furthest from oxygen, configuration depends upon the stereoselectivity (<u>cis</u> or <u>trans</u>) of addition (see structures I, II Figure 4). For alkylation at the internal acetylenic carbon, only one product (structure III, Figure 4) should result, as R and R' must be <u>cis</u>. The electronic and steric environment about the titanium reaction site determined largely by the coordinated ligands would be expected to affect the distribution of these products.

Figure 3.

Pathway for Zeigler Catalysis in the $(RO)_4Ti\text{-}Et_3Al$-ethylene System, R=Et and X=OR

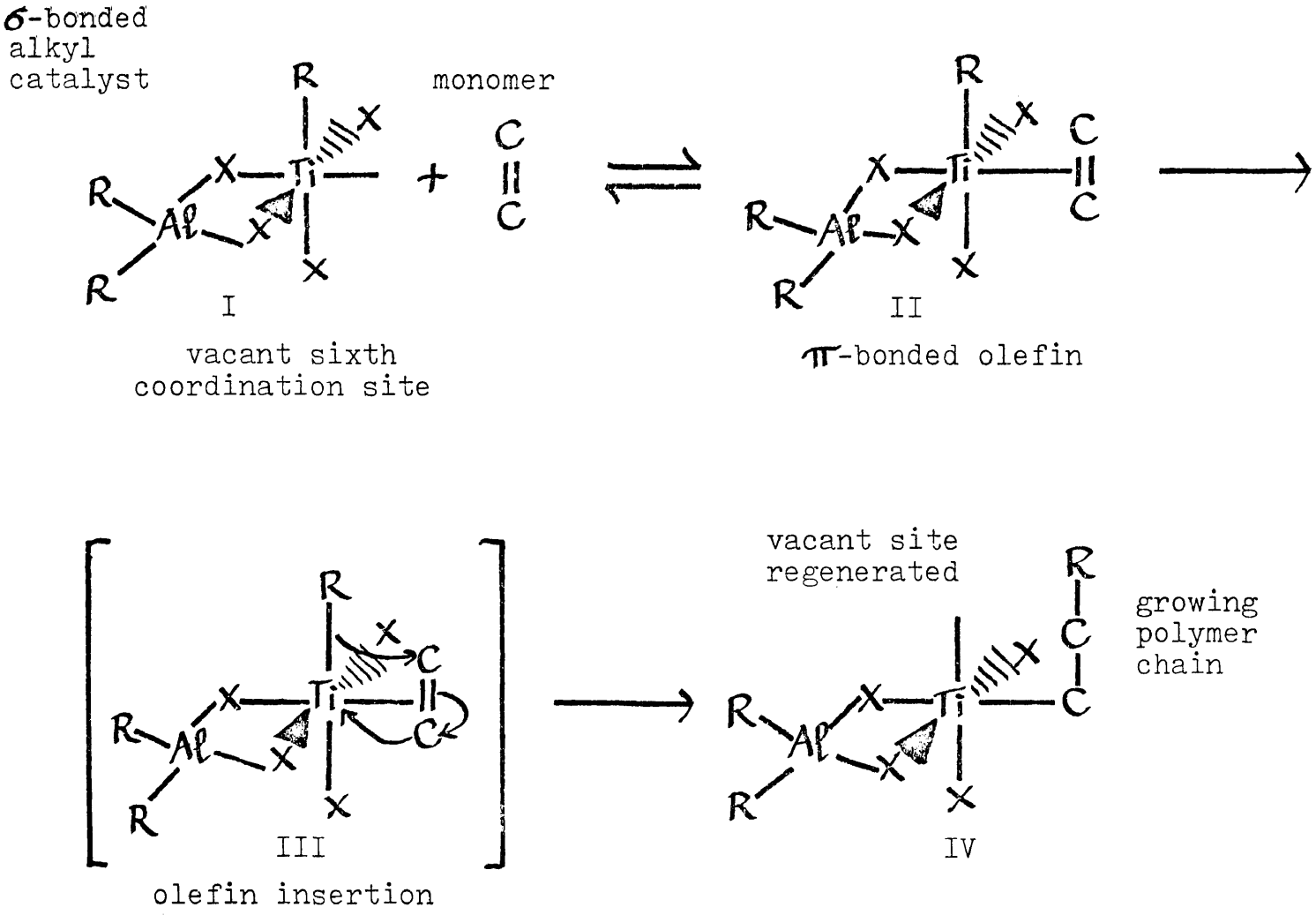
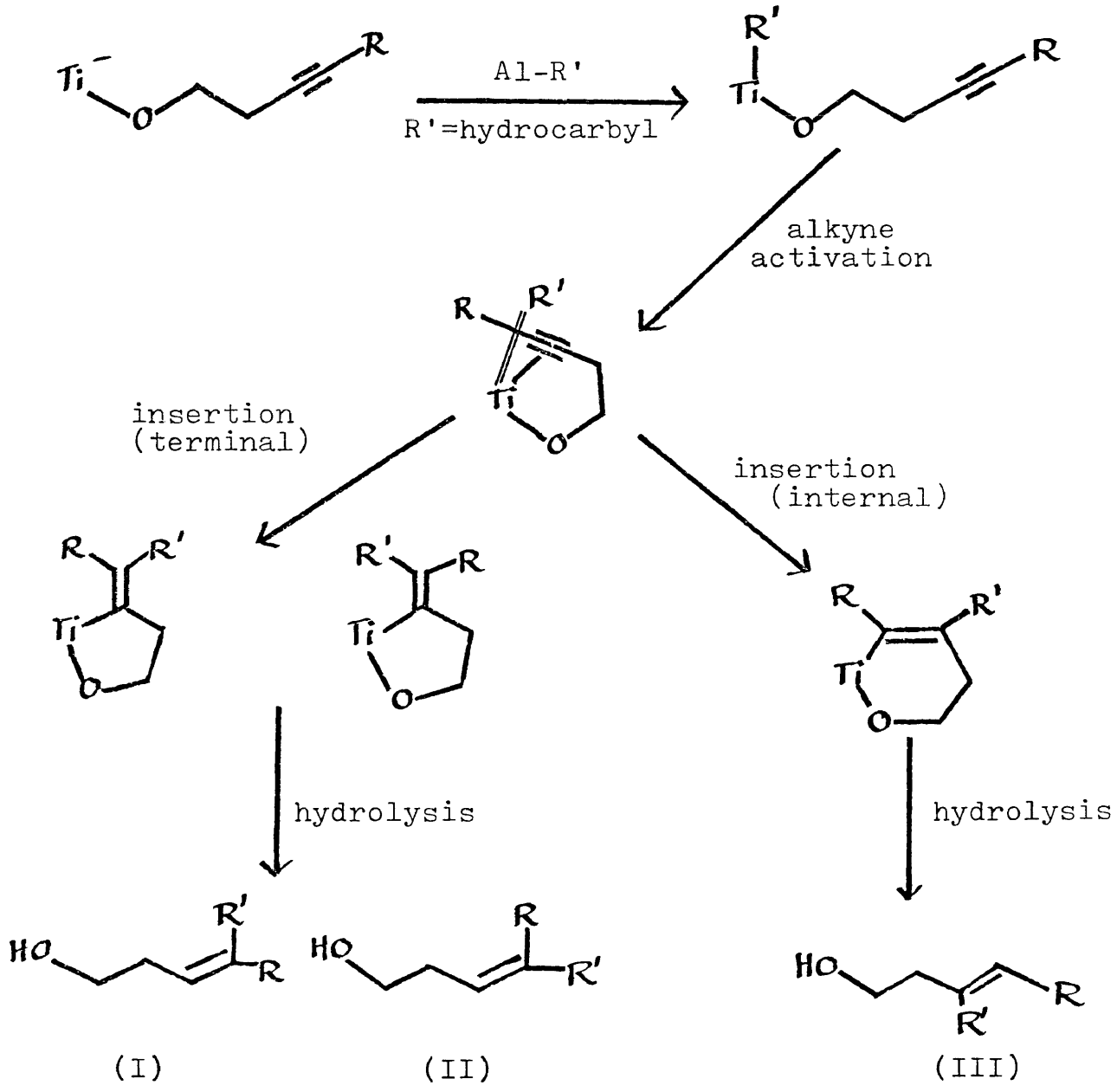


Figure 4.

Adaptation of Zeigler Catalyst System
to Achieve Hydroalkylation of Alkynols



Tweedy, Coleman and Thompson[4] have studied the reaction of cis-chloro(alkynoxy)bis(2,4-pentanedionato)-titanium(IV) complexes with diethylaluminum chloride. Their findings show that a single alkylation product is detected for each of a group of five alkynols. This work will be discussed more thoroughly later.

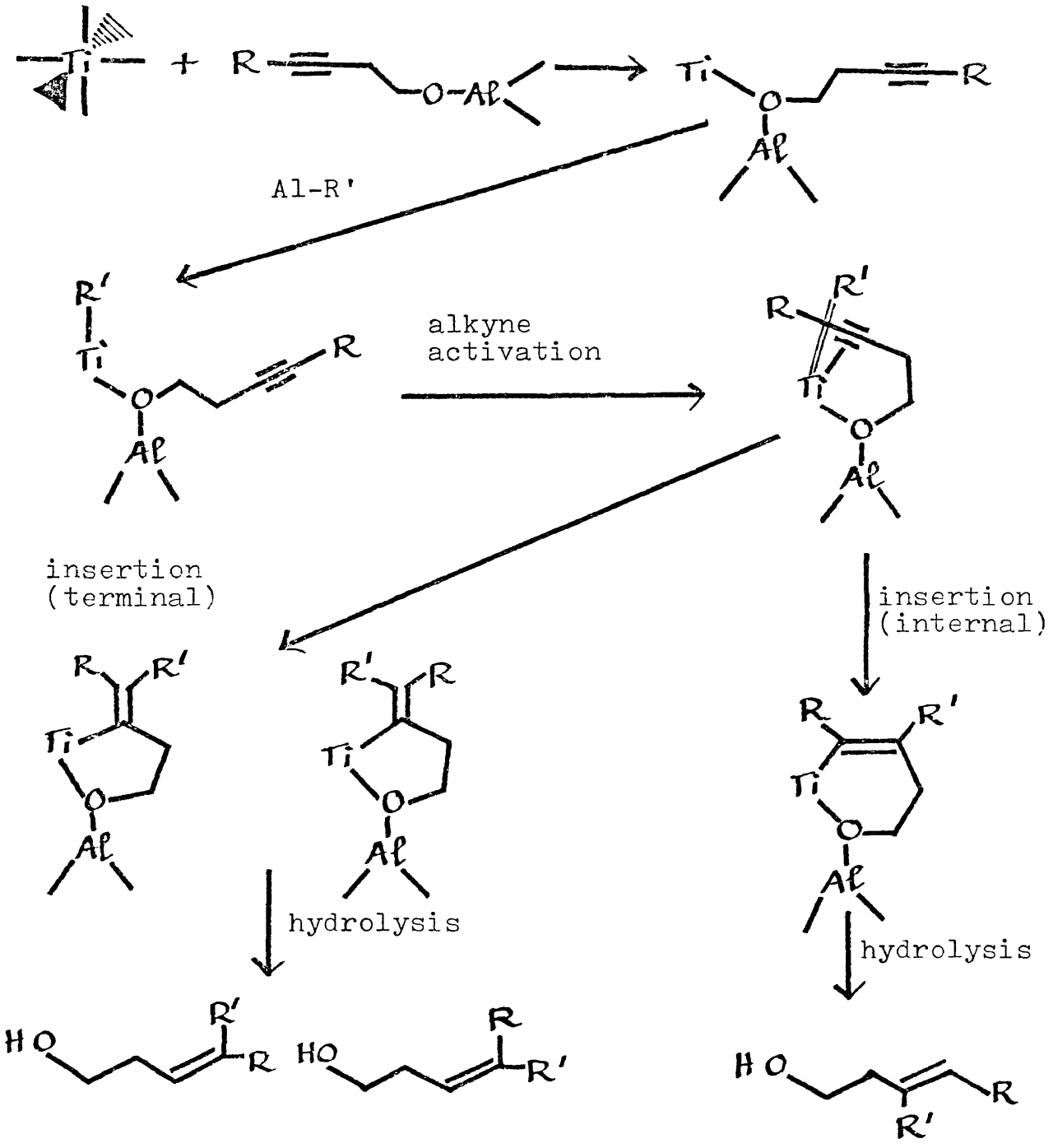
Another approach to utilization of a Zeigler-type system in hydroalkylating alkynols is to react a titanium complex directly with an alkylaluminum alkynoxide. This scheme avoids the toilsome process of preparing the titanium-alkynoxy complex, and is of particular interest if the titanium complex can act in a catalytic manner. As shown in Figure 5, the alkynoxy oxygen could enter into a bridging interaction between the titanium and aluminum atoms. This interaction would bring the alkyne function close to the titanium atom, possibly leading to alkyne activation and subsequent insertion. Hydrolysis would be expected to yield hydroalkylated products of the same structure as produced via the pathway shown in Figure 4.

The second approach to utilization of a Zeigler-type system to the alkynol hydroalkylation problem was utilized in the research herein described. The titanium complex utilized was bis(pentahaptocyclopentadienyl)dichlorotitanium(IV). A series of seven alkynols was studied, each compound being introduced into the reaction scheme as an ethylalkynoxyaluminum chloride·x diethylaluminum chloride adduct (x=1-2.5).

The specific goals of this research were: a) to explore the scope of the mechanism with respect to specific alkynols (terminal, internal, and α substituted), and b) to attempt to optimize yields by varying reaction parameters.

Figure 5.

Reaction of a Titanium Complex with
an Alkyl-(3-alkyn-1-oxy)-aluminum Compound



CHAPTER II

REVIEW OF METAL ASSISTED ALKYNOL ALKYLATION REACTIONS

Grignard Reactions

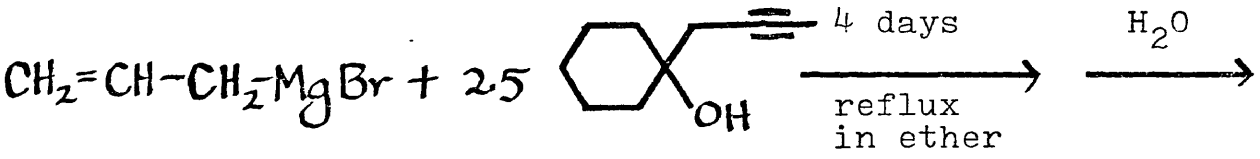
The earliest works relating to metal assisted hydroalkylations of alkynols considered the role of magnesium in Grignard reagent additions to α and β acetylenic alcohols.

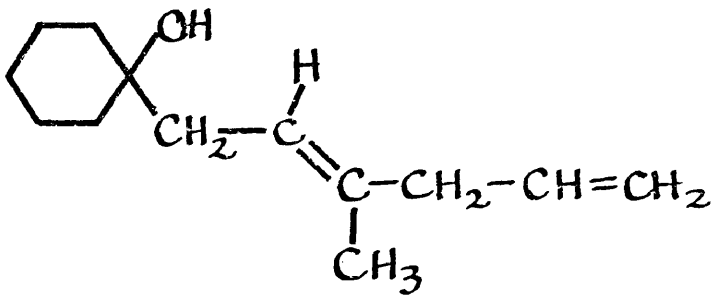
Eisch and Merkley[5], in a preliminary communication, reported that the addition of allylmagnesium bromide to the α acetylenic alcohol 1-(1-propynyl)cyclohexanol and to the β acetylenic alcohol 1-(2-butynyl)cyclohexanol gave hydrolysis products 2-allyl-2-methylvinylidenecyclohexane (80%) and 1-(3-methyl)-2,5-hexadienylcyclohexanol (60%), respectively, after four days of reflux in toluene. The first product was not the expected addition compound. The authors assume that a thermal elimination of MgO (or Mg_2OX_2) occurred during the course of the reaction. The 60% yield in the addition reaction of the β acetylenic alcohol is of the expected addition product which retains its hydroxyl function. Structures I and II of Figure 6 are possible structures for the single product. The cis addition product (I) is judged to be the proper structure, based upon the position (1.58ppm) and coupling constant (J_{AB}=0.9Hz) of the methyl doublet seen in the NMR spectrum. The authors feel that the splitting of the methyl doublet would be much larger (J=1.2-1.7 Hz) for structure II of Figure 6. They are not, however, positive of this structural judgment, as a footnote indicates in their paper.

It was found that the presence of nickel and/or transition metal impurities in the magnesium metal used

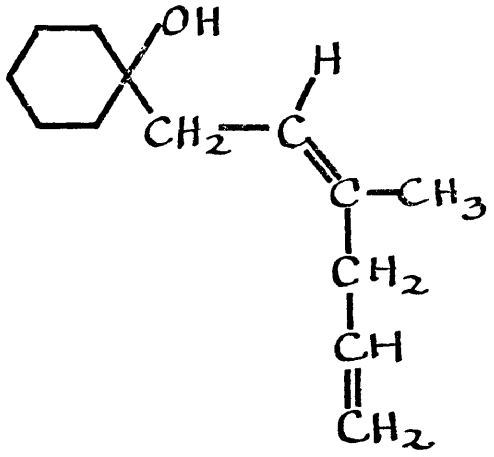
Figure 6.

Addition of Allylmagnesium Bromide to
1-(2-butynyl)-cyclohexanol
from Eisch and Merkley





I



II

for the Grignard reagent promoted the addition of the allylmagnesiumbromide to the acetylenic linkage of the 1-(1-propynyl)cyclohexanol. A somewhat lower yield was achieved using triply sublimed magnesium; this nonetheless lends support to the hypothesis that the allylmagnesium bond can bind unaided to the acetylenic linkage of the aforementioned substrates.

The authors feel that reaction of the alkynols studied with a Grignard reagent is limited, as it is only feasible for highly reactive (i.e. allyl) Grignard reagents within their reaction scheme. Solvent effects did not appear to fit any pattern.

The authors feel that a mechanism compatible with their data involves some form of 'intramolecular coordinative assistance'. (See Figure 7) This model is further supported by the alleged cis addition product resulting from the binding of the organomagnesium to the carbon-carbon triple bond.

Two models, one supporting electrophilic attack of Mg on the π cloud of the acetylenic linkage, and another of electron transfer are proposed to explain the formation of the new bonds in the addition product. (See Figure 8)

In contrast to Eisch and Merkley, two other groups of researchers have proposed a trans addition mechanism for the addition of Grignard reagents to alkynols.

Richey and Von Rein[6], in a communication concurrent with Eisch's, reported addition of allyl Grignard reagents to 2-butyn-1-ol, 3-pentyn-1-ol and 4-phenyl-3-butyn-1-ol. Reaction conditions and yields are tabulated in Table 1. Except for the reaction of 3-pentyn-1-ol with allylmagnesium chloride, all additions yielded a single product. Reasoning that the stereochemistries of carbonated and hydrolyzed products reflect the direction of Grignard reagent additions, the determination of a trans addition mechanism was arrived at through isolation of a lactone produced by

Figure 7.

Intramolecular Coordinative Assistance
from Eisch and Merkley

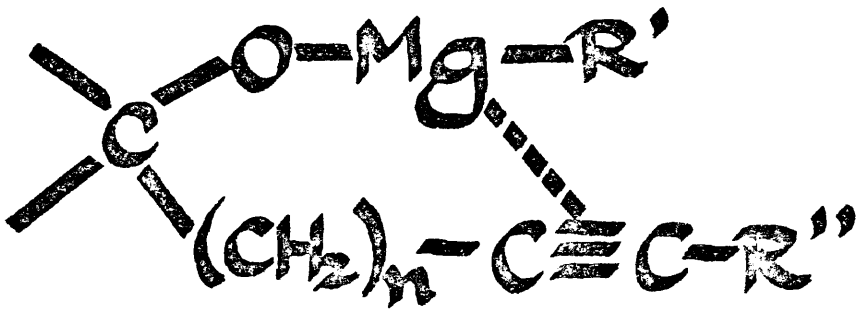
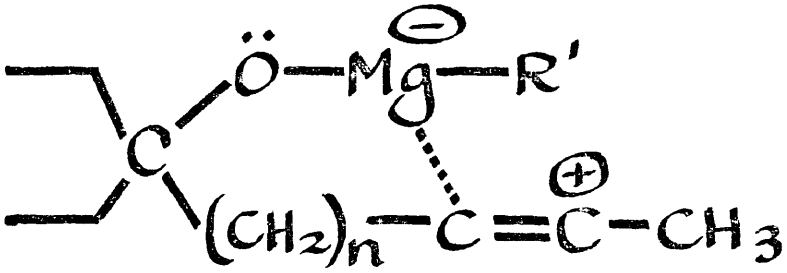


Figure 8.

Models Proposed by Eisch and Merkley
to Explain New Bond Formation

Electrophilic Attack of Magnesium on
the π Cloud of the Acetylenic Linkage



Electron Transfer

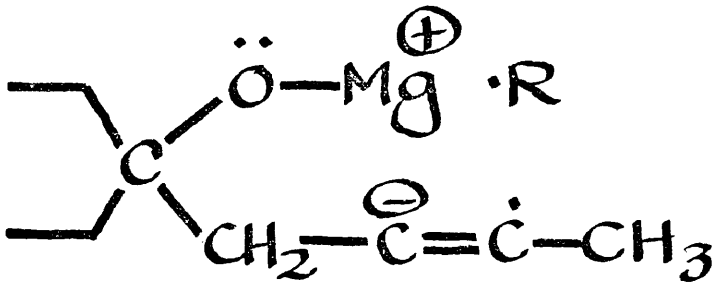
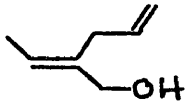
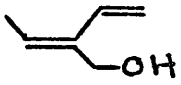
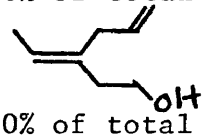
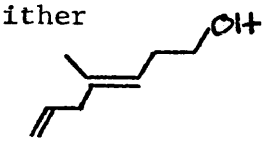
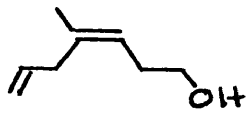
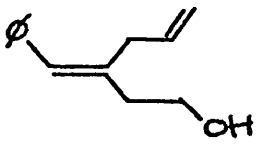


TABLE I
REACTION OF GRIGNARD REAGENTS WITH SELECTED ALKYNOLS
from Richey and Von Rein

Grignard Reagent	Alkynol	Reaction Conditions	Hydrolysis Product(s) Yield (%)
Allyl MgCl	2-butyn-1-ol	Reflux 4 hrs in THF in Ether	75 60 
Vinyl MgCl	2-butyn-1-ol	Reflux 24 hrs in THF	60 
Allyl MgCl	3-pentyn-1-ol	Reflux 4 hrs in Ether	30 total 50% of total  50% of total either  or 
Allyl MgCl	4-phenyl-3-butyn-1-ol	Reflux 4 hrs in Ether	40 

carbonation of the 2-butyn-1-ol allylmagnesium chloride addition product. (See Figure 9) NMR and IR data for structural elucidations were not conclusive.

As reported by Eish, only highly reactive Grignards were found to give products.

Richey and Von Rein are in accord with Eisch concerning the coordinative assistance of oxygen with magnesium in promotion of the additions. However, they feel that an intra or intermolecular trans addition takes place in which the R group is eventually attached to the alkyne carbon closer to the oxygen in a five centered ring. (See Figure 10)

Stepwise formation of the new Mg-C and C-C bonds is postulated as simultaneous bond formation would be sterically improbable. The electron transfer mechanism for Mg-C bond formation proposed by Eisch is considered feasible.

The most recent communication on the subject of Grignard reagent addition to alkynols by Jousseaume and Duboudin[7] notes the effective use of CuI as a catalyst to bring about addition of even mild Grignard reagents. The data presented supports the trans addition theory. Drawing from structural determinations of lactones and 1-oxy-2-sila-3-cyclopentenes derived from the α acetylenic alcohol-Grignard reagent addition products, (see Figure 11) a single trans addition hydrolysis product was formed in all cases but one (see Table II).

Hydrolysis with deuterium oxide confirmed the formation of organomagnesium-vinylic functional intermediates.

Organocopper Reagent Alkylations

Alexis, Normant, and Villieras[8] have investigated the addition of butylcopper-magnesiumbromide reagents to lithium and sodium salts 2-propyn-1-ol, 1-methyl-2-propyn-1-ol and 1,1-dimethyl-2-propyn-1-ol in various solvents under mild conditions (see Table III). The butylcopper reagent is formed via addition of CuBr to a butyl Grignard reagent in

Figure 9.

Trans Product Structure
Deduced from Lactone Structure
from Richey and Von Rein

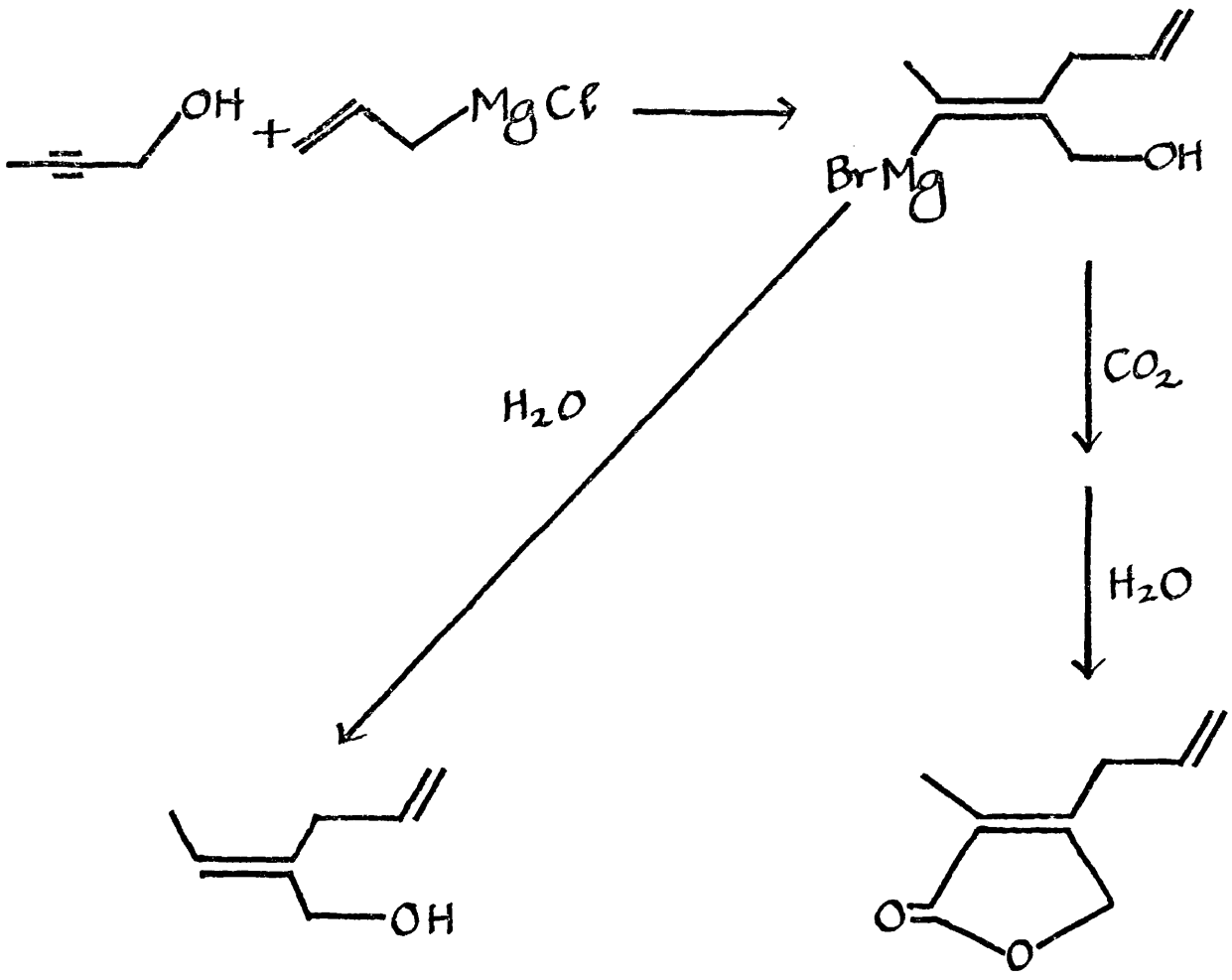
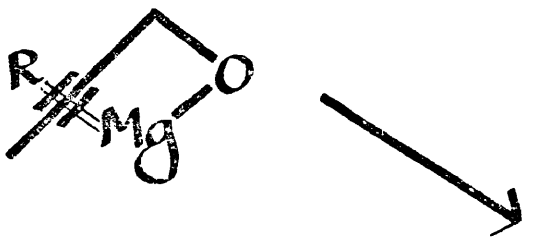
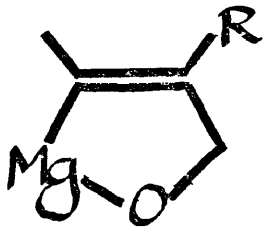


Figure 10.

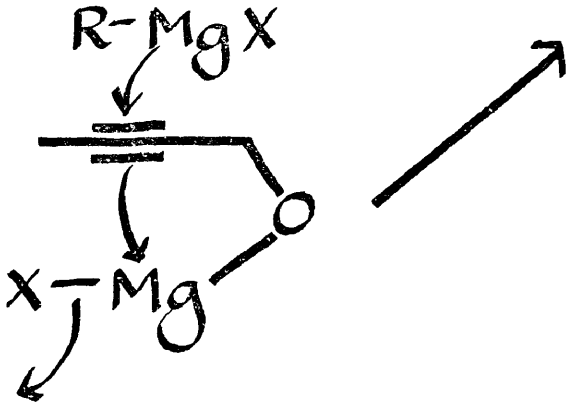
Possible Mechanisms for Trans Addition to C≡C
from Richey and Von Rein

Intramolecular





Intermolecular



Note formation of 5-membered ring.

Figure 11.

Trans Structural Determination by Formation of Lactones and 1-oxy-2-sila-3-cyclopentenes from Jousseame and Duboudin

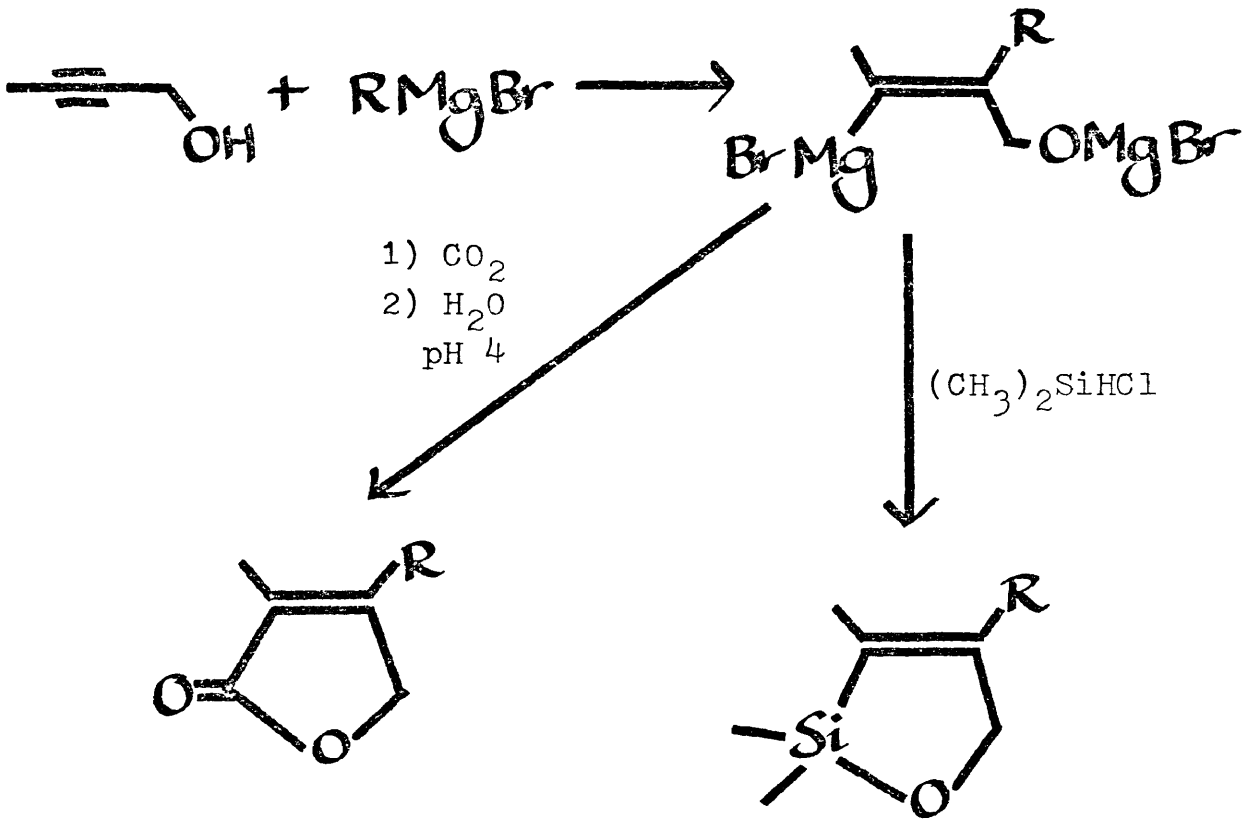


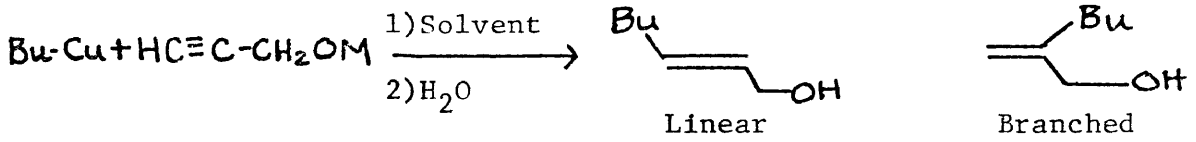
TABLE II
ADDITION OF GRIGNARD REAGENTS TO PRIMARY α-ACETYLENIC ALCOHOLS
WITH CATALYTIC AMOUNT OF CuI
from Jousseaume and Duboudin

Alcohol	RMgBr R=	Yield of β-carbon Alkylated Hydrolysis Product(s) (%)
3-phenyl-2-propyn-1-ol	phenyl-	55
	benzyl-	77
	methyl-	58
	ethyl-	70
	isopropyl-	60
	t-butyl-	55
	allyl-	77
2-propyn-1-ol	phenyl-	73
	benzyl-	80
	methyl-	53
	ethyl-	60
	t-butyl-	45
	allyl-	60
2-butyn-1-ol	phenyl-	40
	isopropyl-	45
	t-butyl-	20
	allyl-	80
	ethyl-	55 total 83% β-alkylated product 17% γ-alkylated product

Organomagnesium (0.6 mol) in ether solution was added to a mixture of CuI (0.02 mol) and acetylenic alcohol (0.2 mol) in ether at 0° under inert atmosphere. The reaction mixture was then stirred at room temperature for several hours.

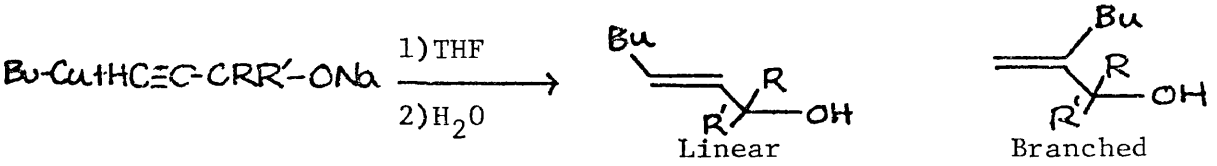
TABLE III
SOLVENT AND STERIC EFFECTS UPON BUTYLCOPPER
ADDITION TO ALCOHOLATES
from Alexis and coworkers

A) Solvent Effect upon Butylcopper Addition to Alcoholates



Temp. (°C)	Time (hrs)	Solvent	M	Yield (total %)	Linear %	Branched %
-10	6	ether	Li	55	40	60
-10	6	THF	Li	68	21	79
-10	6	THF	Na	74	20	80
-10	20	DME	Na	53	13	87
-10	6	HMPT	Na	42	9	91

B) Comparison of 1°, 2°, and 3° Alcoholates in Determining Product Distribution



Alcoholate	R'	R"	Yield (total %)	Linear %	Branched %
1°	H	H	74	24	76
2°	H	Me	56	32	68
3°	Me	Me	46	78	22

ether.

The data presented shows all hydrolysis products to be of the cis addition type. Given this cis addition, two structural isomers are possible, depending on whether the carbon-carbon triple bond is alkylated internally or terminally. Internal alkyl addition leads to a branched product, while terminal alkyl addition gives a linear product. The ratio of branched to linear products for a given reaction appears to be dependent upon both electronic and steric factors.

As a more polar solvent enhances the electronic donor qualities of the oxygen atom, it increases the selectivity of the reaction. The overall yield is somewhat diminished, but the proportion of branched product (internal addition), is increased when the reaction is carried out in a more polar solvent.

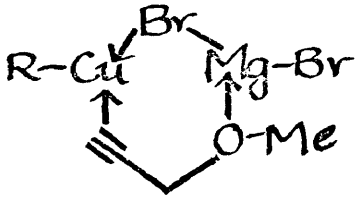
As the alkynol studied progresses from primary to secondary to tertiary, the increasingly crowded conditions favor a terminal addition. This progression leads to a larger proportion of the linear product. The increased crowding also has a diminutive effect on the overall yield of alkynol-butylcopper addition products.

Although β and γ acetylenic alcohols or alcoholates were not studied by Alexis, Normant, and Villieras, some information can be gleaned from the study of molecules such as $HC{\equiv}C\text{-}(CH_2)_n\text{-}Z$ where n=2,3 and Z is an electron rich group such as $S(Et)_2$, OMe, $OSi(Me)_3$, or Br.[8b,9]

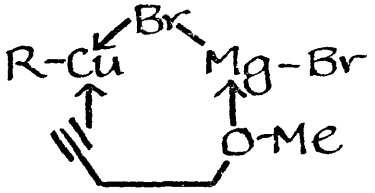
In their study of such molecules, the authors postulate that the linear products are most likely to be formed when a cyclic intermediate can be stabilized through metal-π cloud, and metal-heteroatom coordination (see Figure 12). Also, the highest overall yields are found when the heteroatom has the greatest ability to stabilize the cyclic ring. The ring-stabilizing order of the heteroatoms is determined to be S>N>O>Br.

Figure 12.

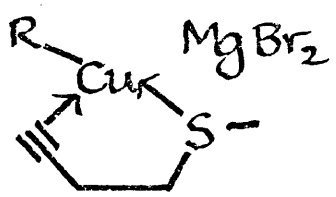
Stable and Unstable Ring Complexes
as Postulated by Alexis, Normant and Villieras



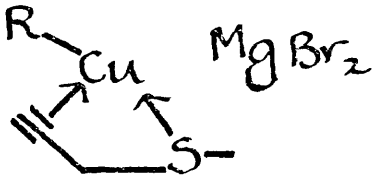
6½ membered ring
(stable)
3% branched products
97% linear products



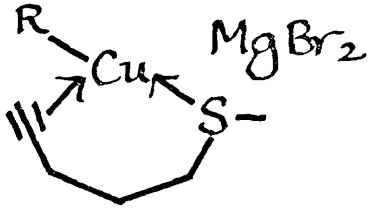
7½ membered ring
(less stable)
89% branched products
11% linear products



5½ membered ring
(possible)
60% branched products
40% linear products



4½ membered ring
(strained)
97% branched products
3% linear products



6½ membered ring
(strained)
95% branched products
5% linear products

Titanium Assisted Organoaluminum Reagent Alkylations

Workers from this laboratory have explored a Zeigler-like system utilizing an alkynoxy-titanium complex and diethylaluminum chloride, to hydroalkylate alkynols under mild conditions[4]. Chloro(alkynoxy)bis(2,4-pentanedionato)-titanium(IV) complexes were prepared via addition of equimolar quantities of alkynol and pyridine to an equal amount of dichlorobis(2,4-pentanedionato)titanium(IV) in a benzene slurry at 0° under inert atmosphere. The mixture was allowed to react for three hours at 0°, then for two hours at room temperature. Pyridinium chloride precipitate was filtered from solution, and the benzene solvent removed under vacuum. The remaining solid or viscous oil was characterized as the desired alkynoxy-titanium complex via low temperature NMR spectra. All complexes characterized were found to possess the cis configuration.

Since the proposed route for alkylation of alkynols is based upon Zeigler-like behavior of the chloro(alcoholate)-bis(2,4-pentanedionato)titanium(IV) complexes (see Figures 3 and 4), one would expect such titanium complexes to function as catalytic components in a Zeigler polymerization system. Indeed, chloro(methoxy)bis(2,4-pentanedionato)titanium(IV)and diethylaluminum chloride were found to be active in polymerizing ethylene. The resultant polymer was linear high density polyethylene as characterized by molecular weight, density, and terminal methyl group data.

The alkynol alkylation reaction conditions were optimized for 3-butyn-1-ol. The remaining alkynols were reacted under the optimized 3-butyn-1-ol system. Results are found in Table IV.

The optimum conditions of reaction at -78° for eight hours with a diethylaluminum:titanium complex ratio of 2:1 as applied to a series of seven alkynols, show that hydrolysis products in moderate yield are produced from β and γ acetylenic alcohols. The addition appears to be

TABLE IV

REACTIONS OF CIS-CHLORO(ALKYNOXY)BIS(2,4-PENTANEDIONATO)TITANIUM(IV) COMPLEXES WITH DIETHYLALUMINUM CHLORIDE

from Tweedy and coworkers

Alkynol as $TiCl(OR)(C_5H_7O_2)_2$	Temperature (°C)	Product yield (%)	Starting alkynol returned (%)	Molar ratio Al:Ti	Reaction time (hr)
3-butyn-1-ol	0	trans-3-hexen-1-ol (28)	2	2:1	4
	-46	trans-3-hexen-1-ol (30)	2	2:1	4
	-78	trans-3-hexen-1-ol (41)	31	2:1	4
	-78	trans-3-hexen-1-ol (19.5)	59.5	2:1	0.25
	-78	trans-3-hexen-1-ol (41)	31	2:1	4
	-78	trans-3-hexen-1-ol (56)	24	2:1	8
	-78	trans-3-hexen-1-ol (49)	30	2:1	10
	-78	trans-3-hexen-1-ol (50)	18.5	2:1	12
	-78	trans-3-hexen-1-ol (3)	75	1:1	4
	-78	trans-3-hexen-1-ol (41)	31	2:1	4
	-78	trans-3-hexen-1-ol (48)	42	3.5:1	4
	-78	trans-3-hexen-1-ol (41)	32	3.5:1	9
2-propyn-1-ol	-78	not analyzed(very small)	13	2:1	8
3-butyn-1-ol	-78	trans-3-hexen-1-ol (56)	24	2:1	8
4-phenyl-3-butyn-1-ol	-78	4-phenyl-3-hexen-1-ol(50)	50	2:1	8
3-pentyn-1-ol	-78	4-methyl-3-hexen-1-ol (44)	21	2:1	8
4-pentyn-1-ol	-78	trans-4-hepten-1-ol (21)	76	2:1	8
4-pentyn-2-ol	-78	trans-4-hepten-2-ol (36)	20		
5-hexyn-1-ol	-78	not analyzed(very small)	96	2:1	8

of an intramolecular cis type; for all compounds characterized, only the linear (terminal addition) product was formed.

The reaction at -78° and 0° of 3-butyn-1-ol with two moles diethylaluminum chloride alone for several hours yielded no hydroalkylated products. This is consistent with the premise that titanium is an essential part of the reaction scheme.

An attempt to produce an active alkynoxy-titanium-aluminum system by first reacting the alkynol with a solution of diethylaluminum chloride to give $Al_2(C_2H_5)_3Cl_2(OR)$ which was then added to cis-dichlorobis(2,4-pentanedionato)-titanium(IV) as per Figure 5 yielded no alkylated products.

Conclusions of Literature Review

The Grignard reagent assisted alkylations of alkynols are useful only for reactive Grignard reagents unless CuI is added in catalytic amounts. Although there is disagreement among researchers whether a cis or trans addition takes place, a single alkylation product is formed in all but two of the reactions sighted. Of the reactions surveyed, α acetylenic alcohols are more reactive than β acetylenic alcohols. Unfortunately, Grignard reagent assisted alkylations of β acetylenic alcohols have not been studied in depth, and analagous alkylations of γ acetylenic alcohols have not been studied at all.

The organocopper assisted alkylations of alkynols yield exclusively cis addition products. Varying proportions of branched to linear structure depend upon the solvent system, electronic and steric factors. The yields reported for α acetylenic alcohols are of a magnitude roughly equivalent to those of the Grignard reagent assisted alkylations. The negative aspect of the organocopper system is, or course, that two products are formed. β and γ acetylenic alcohols were not studied with respect to organocopper assisted alkylations.

The reaction of cis-chloro(alkynoxy)bis(2,4-pentanedionato)titanium (IV) with diethylaluminum chloride presents a useful approach to the stereospecific alkylation of β and γ acetylenic alcohols. All products characterized were of the cis-addition type, and were exclusively trans isomers. Reasoning from the Zeigler catalyst systems, it would seem possible to develop syntheses using catalytic amounts of a titanium complex.

This research was undertaken to explore a different titanium-alkynoxy-alkyl-aluminum system, utilizing a procedure which would permit catalytic amounts of dichlorobis-(pentahaptocyclopentadienyl)titanium(IV) to interact with selected alkynols. By introducing the alkynol into the reaction scheme as ethylalkynoxyaluminum chloride x diethylaluminum chloride adduct (x=1-2.5), it was hoped to avoid the toilsome preparation of a titanium-alkynoxy complex, and to explore stoichiometric relationships not possible using a preformed titanium-alkynoxy complex. Also, the presence of ligands about the titanium different from those utilized by Tweedy et al., might be expected to have some effect upon product distribution and stereochemistry.

CHAPTER III

EXPERIMENTAL

Solvents

Methylene chloride (dichloromethane) was acquired from Fischer Scientific Company. The solvent, "Certified A.C.S.", was redistilled over phosphorous pentoxide under dry N_2 flow, then stored over Linde 4-A molecular sieves under N_2.

Benzene was acquired from Fischer Scientific Company. The solvent, "Certified A.C.S.", was redistilled over calcium hydride under N_2, then stored over Linde 4-A molecular sieves under N_2.

"Laboratory Grade" ether also from Fischer, was utilized for extractions without additional preparation. Methanol "Certified A.C.S." from Fischer, was also utilized without additional preparation.

Sulfuric acid solution (5% by volume) saturated with sodium chloride in distilled water was prepared with sulfuric acid ("Reagent A.C.S." 95.0-98.0%) acquired from Fischer Scientific Company, sodium chloride, "Certified A.C.S." from Fischer, and distilled water.

Reagents

Diethylaluminum chloride solutions (approximately 2 Molar) were prepared from diethylaluminum chloride obtained from Ethyl Corporation, and methylene chloride from Fischer (prepared as described above).

Commercially acquired reagents, listed with source and purity if available:

dichlorobis(pentahaptocyclopentadienyl)titanium(IV)	Strem Chemicals Alfa Products	
2-propyn-1-ol	Eastman Organic Chemicals	redistilled
3-butyn-1-ol	Farchan Division	gc 99%
4-pentyn-1-ol	Farchan Division	
4-pentyn-2-ol	Farchan Division	gc 99%
3-pentyn-1-ol	Farchan Division	gc 99%
5-hexyn-1-ol	Farchan Research Labs	gc 99%
4-phenyl-3-butyn-1-ol	Farchan Division	gc 99%
trans-3-hexen-1-ol	Chemical Samples	98%
n-butanol	Aldrich Chemical Co.	gc, ir
n-hexanol	Aldrich Chemical Co.	gc, ir 98%
n-heptanol	Eastman Organic Chemicals	
n-octanol	Fischer Scientific Co.	Certified
n-decanol	Eastman Organic Chemicals	
deuterium oxide	Diaprep, Inc.	ir, nmr 99.7%
magnesium sulfate anhydrous	Fischer Scientific Co.	Certified
Celite	Fischer Scientific Co.	

Generalized Reaction Procedure

All reactions took place in apparatus which had been dried in an oven at 110°, assembled and flamed under argon before any reagents were introduced. All glass syringes used to transfer reagents were also dried in an oven, then

flushed with argon before use. Plastic syringes were used to transfer alkynols to the dropping funnel without any such heating.

A. Preparation of alkynoxy(ethyl)aluminum chloride-diethylethylaluminum chloride reagents

A 250 ml, three necked round bottomed flask was equipped with a 50 ml dropping funnel with adapter, a condenser, a teflon coated stirring bar, and a rubber septum (see Figure 13). The system was attached to an argon flow equipped with an oil bubbler.

Methylene chloride (75 ml) was added via syringe to the round bottomed flask. Methylene chloride (25 ml) was added to the dropping funnel in the same fashion.

Approximately either 20 or 40 millimoles of the alkynol was added to the dropping funnel via syringe. An accurate measure of the amount of alkynol was accomplished by weighing the syringe before and after the alkynol was added.

Enough diethylaluminum chloride (approximately 2 Molar methylene chloride solution) was added to the round bottomed flask via syringe to give the desired ratio of diethylaluminum chloride to alkynol.

The round bottomed flask was then inserted into an ice bath, stirred, and allowed to reach thermal equilibrium. The alkynol solution was then added dropwise to the stirring diethylaluminum chloride solution over a period of one-third to one-half hour.

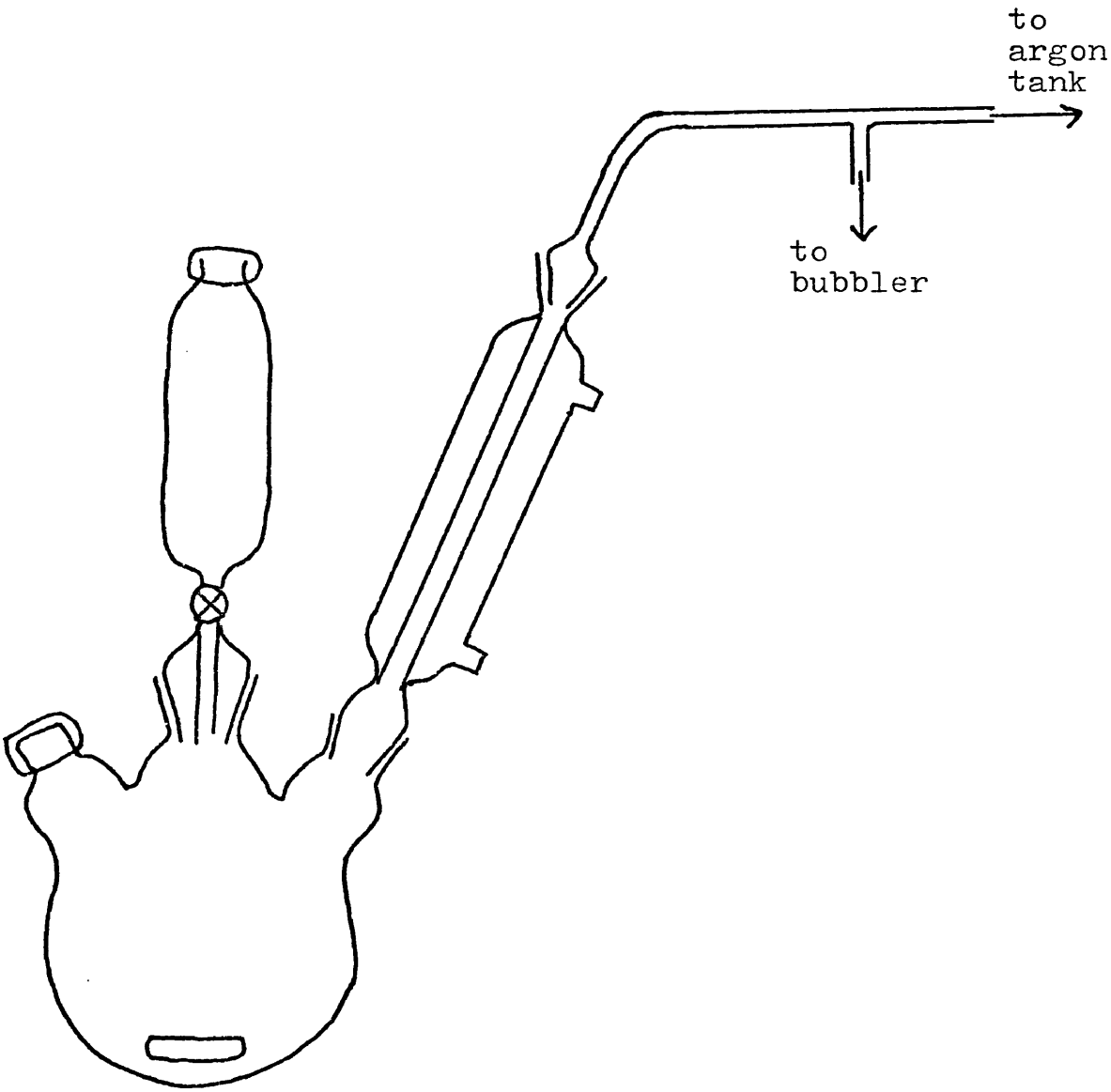
The organoaluminum product solution was maintained at 0^{o} until needed. It was always used within two hours of the end of the alkynol addition.

B. Reaction of alkynoxy(ethyl)aluminum chloride-diethylaluminum chloride reagent with dichlorobis(pentahaptocyclopentadienyl)titanium(IV)

One or two glassware setups identical to that used in part A were constructed. Methylene chloride (50 ml) and the appropriate amount of dichlorobis(pentahaptocyclopen-

Figure 13.

Apparatus for Generalized Reaction Procedure



tadienyl)titanium(IV) were added to each round bottomed flask.

The round bottomed flasks were placed in an ice bath or other low temperature bath and allowed to achieve thermal equilibrium. If twenty millimoles of alkynol were initially reacted, the total volume of the organoaluminum product was transferred to a single dropping funnel. If forty millimoles of the alkynol were initially reacted, then one-half of the organoaluminum product was transferred to each of the dropping funnels of the individual setups. The transfer was made via syringe. The organoaluminum was then added dropwise to the stirring titanium complex solution over a period of 0.3 to 0.7 hour. If the reaction flasks were maintained at the low temperature of addition, the reaction duration was counted from the beginning of the organoaluminum addition. If, however, the reaction flask was allowed to reach room temperature or reflux after the addition, reaction time was counted from the end of the organoaluminum addition.

Predetermined reaction temperature and duration were maintained for the stirring mixture.

The reaction was terminated at 0^{o} or below with dropwise addition of 5 ml methanol, then 50 ml 5%H_2SO_4/H_2O/saturated NaCl solution to the stirring reaction mixture. This hydrolysis could be quite vigorous; caution was necessary to keep the reaction mixture from spouting through the gas lines. After hydrolysis, the reaction mixture could be exposed to the atmosphere and argon flow was no longer necessary.

C. Isolation of products for analysis.

The product solution was transferred from the round bottomed flask to a 500 ml Erlenmeyer flask with 50 ml rinse of 5%H_2SO_4/H_2O/saturated NaCl solution. If the color of the product solution had changed from the characteristic deep red of the dichlorobis(pentahaptocyclo-

pentadienyl)titanium(IV), oxygen was flowed over the stirring solution until it darkened. This was done to oxidize any titanium which had been reduced.

As the product solution almost always had some precipitate present, it was filtered through a 1/8 inch bed of Celite via a Buchner funnel with H_2O and methylene chloride, or H_2O and ether rinses.

The product filtrate was saturated with sodium chloride, then extracted with five 50 ml fractions of ether. The ether fractions were combined and then dried over anhydrous magnesium sulfate.

The dried ether fractions were filtered through fluted paper into a 500 ml round bottomed flask with a boiling chip. The round bottomed flask was then attached to a rotary evaporator in a warm water bath and reduced to a volume appropriate for gas chromatographic analysis.

If the amount of titanium complex used in a reaction was large, a large amount of solid would sometimes begin to precipitate out before all the ether had been pulled by the rotary evaporator. In these cases, the product solution and precipitate (usually constituting about 10 ml) were refiltered through fluted paper with five 20 ml fractions of ether rinse into a dry 200 ml round bottomed flask. This solution was then reduced to the appropriate volume on the rotary evaporator.

Recoverability Experiments

In order to determine the effect of experimental technique on the recoverability of products and byproducts in the alkynol hydroalkylation reactions, mixtures of n-butanol and n-hexanol were subjected to the reaction procedure. Since n-butanol and n-hexanol are saturated alcohols, they should undergo no reaction and be returned to the final product sample in a percentage of their original proportions which would be the recoverability of compounds of similar structure.

Reaction 1. N-butanol (0.7788g, 10.51 mmol) and n-hexanol (1.0351g, 10.14 mmol) were added to 32 ml of 1.64 M solution of diethylaluminum chloride (250 mole % with respect to the combined amount of alcohols) according to the generalized procedure. The organoaluminum product was added to a solution of 50 mole % Cp_2TiCl_2 (2.57 g) at 0^o and reacted for two hours as per generalized procedure. The final product sample, prepared according to the generalized procedure was deep red with a fine red precipitate.

Reaction 2. N-butanol (0.7190g, 9.700 mmol) and n-hexanol (1.0280g, 10.060 mmol) were added to 30 ml of 1.635 M solution of diethylaluminum chloride (250 mole % with respect to the combined amount of alcohols) according to the generalized procedure. The organoaluminum product was added to a solution of 50 mole % Cp_2TiCl_2 (2.46 g) at 0^o and reacted for two hours as per generalized procedure. The final product sample, prepared according to the generalized procedure, was deep red with a fine red precipitate.

Alkynol Hydroalkylation Reactions

Reaction Group I. Ethylation of 3-Butyn-1-ol with Diethylaluminum Chloride

Reaction I-1. 3-butyn-1-ol (2.957g, 42.20 mmol) was added to 57 ml of 1.85 M solution of diethylaluminum chloride (250 mole %) according to the generalized reaction procedure.

Reaction I-1-a. One half (21.10 mmol) of the organoaluminum product was added to a solution of 50 mole % Cp_2TiCl_2 (2.63 g) according to the generalized procedure at 0^o and reacted for six hours. The product sample was terminated and prepared using a base hydrolysis (substituting 6 N NaOH for all 5% H_2SO_4 solutions). The final product sample was yellow with a fine yellow precipitate.

Reaction I-1-b. One half (21.10 mmol) of the

organoaluminum product was added to a solution of 50 mole % Cp_2TiCl_2 (2.63 g) according to the generalized procedure at -78° and reacted for six hours. The reaction was terminated and the product sample was prepared using a base hydrolysis (substituting 6 N NaOH for all 5% H_2SO_4 solutions). The final product solution was orange.

Reaction I-2. 3-butyn-1-ol (2.8418g, 40.50 mmol) was added to 55 ml of 1.85 M diethylaluminum chloride solution (250 mole %) according to the generalized reaction procedure.

Reaction I-2-a. One half (20.25 mmol) of the organoaluminum product was added to a solution of 50 mole % Cp_2TiCl_2 (2.52 g) at -22° and reacted for 5.75 hours as per the generalized procedure. The final product sample was deep red with a fine red precipitate.

Reaction I-2-b. This reaction was the same as I-2-a except that the reaction took place at reflux for 5.5 hours. The final product sample was deep red with a yellow-orange precipitate.

Reaction I-3. 3-butyn-1-ol (2.7754g, 39.60 mmol) was added to 61 ml of 1.635 M solution of diethylaluminum chloride (250 mole %) according to the generalized reaction procedure.

Reaction I-3-a. One half (19.80 mmol) of the organoaluminum product was added to a solution of 10 mole % Cp_2TiCl_2 (0.49 g) at 0° and reacted according to the generalized reaction procedure for six hours. The product sample was deep red with a fine red precipitate.

Reaction I-3-b. The second half of the organoaluminum reagent was treated the same as in I-3-a except that 25 mole % of Cp_2TiCl_2 (1.23 g) was used. The final product sample was deep red with a fine red precipitate.

Reaction I-4. 3-butyn-1-ol (2.8929g, 41.27 mmol) was added to 45 ml of 2.3 M diethylaluminum chloride (250 mole %) according to the generalized reaction pro-

cedure.

Reaction I-4-a. One half (20.63 mmol) of the organoaluminum product was added to a solution of 10 mole % Cp_2TiCl_2 (0.51 g) according to the generalized reaction procedure at 0° and reacted for six hours. The final product sample was deep red with a fine red precipitate.

Reaction I-4-b. One half of the organoaluminum reagent was treated the same as I-4-a except that 25 mole % of Cp_2TiCl_2 (1.28 g) was used. The final product sample was deep red with a fine red precipitate.

Reaction I-5. 3-butyn-1-ol (2.7794g, 39.655 mmol) was added to 47 ml of 2.1 M solution of diethylaluminum chloride (250 mole %) according to the generalized reaction procedure.

Duplicate Reactions I-5-a and I-5-b. One half (19.828 mmol) of the organoaluminum product was added to a solution of 10 mole % Cp_2TiCl_2 (0.49 g) according to the generalized procedure at 0° and reacted for 0.25 hours past addition. Total reaction time was .75 minutes. The final product sample was deep red-orange with a fine red precipitate.

Reaction I-6. 3-butyn-1-ol (2.7438g, 39.147 mmol) was added to 18.6 ml of 2.1 M diethylaluminum chloride (100 mole %) according to the generalized reaction procedure.

Duplicate Reactions I-6-a and I-6-b. One half of the organoaluminum product (19.574 mmol) was added to a solution of 10 mole % Cp_2TiCl_2 (0.49 g) according to the generalized procedure at 0° and reacted for 6 hours. The final product sample was deep red with a fine red precipitate.

Reaction I-7. 3-butyn-1-ol (2.8020g, 39.977 was added to 33 ml of 2.1 M diethylaluminum chloride (175 mole %) according to the generalized reaction procedure.

Duplicate Reactions I-7-a and I-7-b. One half of

the organoaluminum product (19.989 mmol) was added to a solution of 10 mole % Cp_2TiCl_2 (0.50g) according to the generalized procedure at 0° and reacted for 6 hours. The final product sample was deep red with a fine red precipitate.

Reaction I-8. 3-butyn-1-ol (2.6596g, 37.945 mmol) was added to 45 ml of 2.1 M diethylaluminum chloride (250 mole %) according to the generalized reaction procedure.

Duplicate Reactions I-8-a and I-8-b. One half (18.973 mmol) of the organoaluminum product was added to a solution of 10 mole % Cp_2TiCl_2 (0.47 g) according to the generalized reaction procedure at 0° and reacted for 4 hours. Hydrolysis of the reaction was accomplished with dropwise addition of 5 ml D_2O followed by one half hour of stirring before addition of 50 ml of 5% H_2SO_4/H_2O/saturated NaCl solution. The final product sample was deep red with a fine red precipitate.

Reaction I-9. 3-butyn-1-ol (2.8140g, 40.148 mmol) was added to 45 ml of 2.23 ml diethylaluminum chloride (250 mole %) according to the generalized reaction procedure, except that benzene rather than methylene chloride was used as the solvent.

Duplicate Reactions I-9-a and I-9-b. One half of the organoaluminum product (20.074 mmol) was added to a solution of 10 mole % Cp_2TiCl_2 (0.50 g) according to the generalized reaction procedure except that benzene rather than methylene chloride was used as the solvent, at 0° and reacted for 6 hours. The final product sample was red-orange.

Reaction I-10. 3-butyn-1-ol (2.7571g, 39.377 mmol) was added to 58 ml of 1.69 M diethylaluminum chloride (250 mole %) according to the generalized reaction procedure.

Duplicate Reactions I-10-a and I-10-b. One half of the organoaluminum product (19.669 mmol) was added to a solution of 10 mole % (0.49 g) according to the gener-

alized reaction procedure at 0° and reacted for 2 hours. The final product sample was deep red-orange with a fine red precipitate.

Reaction I-11. 3-butyn-1-ol (2.8221g, 40.264 mmol) was added to 44 ml of 2.27 M diethylaluminum chloride (250 mole %) according to the generalized reaction procedure.

Duplicate Reactions I-11-a and I-11-b. One half of the organoaluminum product (20.132 mmol) was added to a solution of 25 mole % dichlorobis(pentahaptocyclopentadienyl)zirconium(IV) (1.47 g), instead of Cp_2TiCl_2, according to the generalized reaction procedure at 0° and reacted at room temperature for 6 hours. The final product sample was faint yellow with a white precipitate.

Reaction Group II. Ethylation of 4-Pentyn-2-ol with Diethylaluminum Chloride

All reactions in this group utilized 250 mole % diethylaluminum chloride, and all final product samples were deep red with a fine red precipitate.

Reaction II-1. 4-pentyn-2-ol (2.9489g, 35.052 mmol) was added to 39 ml of 2.23 M diethylaluminum chloride according to the generalized reaction procedure.

Duplicate Reactions II-1-a and II-1-b. One half of the organoaluminum product (17.526 mmol) was added to a solution of 10 mole % Cp_2TiCl_2 (0.44 g) according to the generalized reaction procedure at 0° and reacted for 4 hours.

Reaction II-2. 4-pentyn-1-ol (3.2412g, 38.526 mmol) was added to 42 ml of 2.27 M diethylaluminum chloride according to the generalized reaction procedure.

Duplicate Reactions II-2-a and II-2-b. One half of the organoaluminum product (19.263 mmol) was added to a solution of approximately 10 mole % Cp_2TiCl_2 (approximately 0.5 g weighed out in a dry box) at -35° and reacted for 4.7 hours according to the reaction procedure.

Reaction II-3. 4-pentyn-2-ol (3.1723g, 37.707 mmol) was added to 41 ml of 2.27 M diethylaluminum chloride according to the generalized reaction procedure.

Duplicate Reactions II-3-a and II-3-b. One half of the organoaluminum product (18.854 mmol) was added to a solution of approximately 10 mole % Cp_2TiCl_2 (approximately 0.5 g weighed out in a dry box) according to the generalized reaction procedure at 0° then reacted at room temperature for 4 hours.

Reaction II-4. 4-pentyn-2-ol (3.3686g, 40.040 mmol) was added to 44 ml of 2.27 M diethylaluminum chloride according to the generalized reaction procedure.

Duplicate Reactions II-4-a and II-4-b. One half of the organoaluminum product (20.020 mmol) was added to a solution of approximately 55 mole % Cp_2TiCl_2 (approximately 2.8 g weighed out in a dry box) according to the generalized reaction procedure at 0° and reacted for 4 hours.

Reaction Group III. Ethylation of 4-Pentyn-1-ol with Diethylaluminum Chloride

All reactions in this group utilized 250 mole % diethylaluminum chloride, and all final product samples were deep red with a fine red precipitate.

Reaction III-1. 4-pentyn-1-ol (1.8118g, 21.536 mmol) was added to 27 ml of 2.00 M diethylaluminum chloride according to the generalized reaction procedure. The organoaluminum product (21.536 mmol) was added to a solution of 10 mole % (0.54 g) Cp_2TiCl_2 according to the generalized reaction procedure at 0° and reacted for 4 hours.

Reaction III-2. 4-pentyn-1-ol (3.3491g, 39.809 mmol) was added to 44 ml of 2.27 M diethylaluminum chloride according to the generalized reaction procedure.

Duplicate Reactions III-2-a and III-2-b. One half of the organoaluminum product solution (19.904 mmol) was added to a solution of approximately 50 mole % Cp_2TiCl_2

(approximately 2.2 g weighed out in a dry box) according to the generalized reaction procedure at 0° and reacted for 4 hours.

Reaction Group IV. Ethylation of 3-Pentyn-1-ol with Diethylaluminum Chloride

All reactions of this group utilized 250 mole % diethylaluminum chloride, and all final product samples were deep red-orange with a fine red precipitate.

Reaction IV-1. 3-pentyn-1-ol (3.3395g, 39.695 mmol) was added to 50 ml of 2.0 M diethylaluminum chloride according to the generalized reaction procedure.

Duplicate reactions IV-1-a and IV-1-b. One half of the organoaluminum product (19.849 mmol) was added to a solution of 10 mole % Cp_2TiCl_2 (0.49 g) according to the generalized reaction procedure at 0° and reacted for 4 hours.

Reaction IV-2. 3-pentyn-1-ol (2.4896g, 29.592 mmol) was added to 37 ml of 2.0 M diethylaluminum chloride according to the generalized reaction procedure.

Duplicate reactions IV-2-a and IV-2-b. One half of the organoaluminum product (14.796 mmol) was added to a solution of 25 mole % Cp_2TiCl_2 (0.92 g) according to the generalized reaction procedure at 0° and reacted for 4 hours.

Reaction IV-3. 3-pentyn-1-ol (2.8640g, 34.043 mmol) was added to 38 ml of 2.27 M diethylaluminum chloride according to the generalized reaction procedure.

Duplicate Reactions IV-3-a and IV-3-b. One half of the organoaluminum product (17.022 mmol) was added to a solution of approximately 50 mole % Cp_2TiCl_2 (approximately 2.2 g weighed out in a dry box) according to the generalized reaction procedure at 0° and reacted for 4 hours.

Reaction Group V. Ethylation of 4-Phenyl-3-butyn-1-ol with Diethylaluminum Chloride

All reactions in this group utilized 250 mole %

diethylaluminum chloride, and all final product samples were deep red with a fine red precipitate.

Reaction V-1. 4-phenyl-3-butyn-1-ol (5.8399g, 39.947 mmol) was added to 50 ml of 2.0 M diethylaluminum chloride according to the generalized reaction procedure.

Duplicate Reactions V-1-a and V-1-b. One half of the organoaluminum product (19.974 mmol) was added to a solution of 20 mole % Cp_2TiCl_2 (1.0 g) according to the generalized reaction procedure at 0°, reacted at 0° for approximately 8 hours until the ice melted, then maintained at room temperature for a total reaction time from addition of 16.5 hours.

Reaction V-2. 4-phenyl-3-butyn-1-ol (6.2192g, 42.542 mmol) was added to 47 ml of 2.27 M diethylaluminum chloride according to the generalized reaction procedure.

Duplicate reactions V-2-a and V-2-b. One half of the organoaluminum product (21.271 mmol) was added to a solution of approximately 50 mole % Cp_2TiCl_2 (approximately 2.5 g weighed out in a dry box) according to the generalized procedure at 0° and reacted for 4 hours.

Reaction Group VI. Ethylation of 2-Propyn-1-ol with Diethylaluminum Chloride

Reaction VI-1. 2-propyn-1-ol (2.0278g, 36.166 mmol) was added to 41 ml of 2.23 M diethylaluminum chloride (250 mole %) according to the generalized reaction procedure.

Duplicate Reactions VI-1-a and VI-1-b. One half of the organoaluminum product (18.083 mmol) was added to a solution of 10 mole % Cp_2TiCl_2 (0.45 g) according to the generalized reaction procedure at 0° and reacted for 4 hours. The final product sample was deep brown.

Reaction Group VII. Ethylation of 5-Hexyn-1-ol with Diethylaluminum Chloride

Reaction VII-1. 5-hexyn-1-ol (3.4519g, 35.173 mmol) was added to 44 ml of 2.0 M diethylaluminum chloride

(250 mole %) according to the generalized reaction procedure.

Duplicate Reactions VII-1-a and VII-1-b. One half of the organoaluminum product (17.587 mmol) was added to a solution of 10 mole % Cp_2TiCl_2 (0.44 g) according to the generalized reaction procedure at 0° and reacted for 4 hours. The final product sample was deep red-orange with a fine red precipitate.

Analytical Techniques

Gas-Liquid Phase Chromatography

Gas-liquid phase chromatography is a valuable tool for determining both quantitative and qualitative features of the compounds found in a product sample.

Two gas chromatographs were used during the course of this research: 1) F and M Model 720, and 2) Hewlett Packard Model 5750.

The columns used and their application to this research:

1) 10% Carbowax	(6'x1/4")	20M on 60-80W Low	Preparative
2) 10% XE-60	(8'x1/8")	on 80/100 chromosorb WHP E2508 Supelco	Qualitative Quantitative
3) 10% Carbowax	(8'x1/4")	20M on 80/100 chromosorb WHP E2508 Supelco	Qualitative Quantitative
4) 10% XE-60	(2'x1/4")	Silicon Gum Rubber	Preparative

Three types of standards were used in the chromatographic work.

Qualitative Standard. A qualitative standard consists of a small amount of a specific compound which is added to an aliquot of a reaction product sample. If the specific compound was initially present in the sample, one of the peaks would simply enlarge. If the

specific compound was not present in the mixture, a new peak would appear. Qualitative standards provided information relating to the retention time of specific compounds on various columns and provided evidence, though not conclusive, for specific reaction products.

Quantitative Standard. A quantitative standard mixture contained authentic samples of expected products and by-products of a specific reaction. In addition, an internal standard (described later) was present in the mixture. The weight of each compound of the mixture was precisely determined. Upon analysis of several injections of the quantitative standard mixture, response factors were determined for each compound relative to the internal standard.

In some cases, authentic product samples were not available. Compounds of similar structure and nearly identical retention time were then used to estimate the proper response factor. The products for which authentic samples were not available in sufficient quantity, and the compounds used to determine the proper response factors are presented in Figure 14.

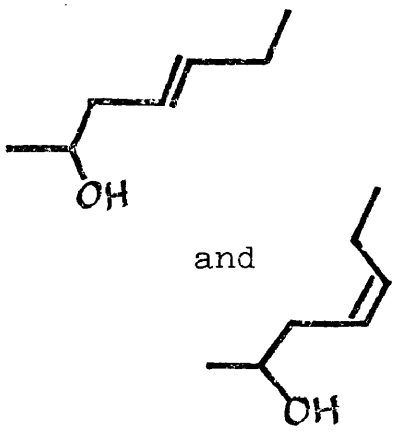
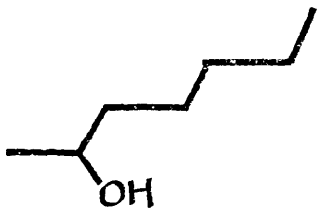
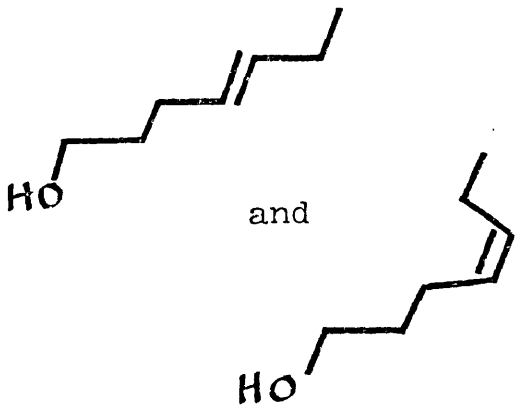
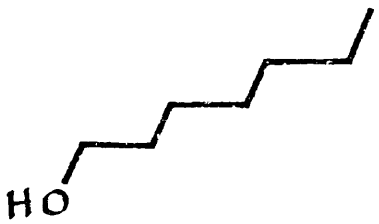
Internal Standard. An internal standard is a specific compound selected for addition to reaction product samples (either a quantitative standard mixture, or to the products of an actual experimental run) in order to determine the quantitative yield of product(s). An internal standard with a retention time significantly different from that of the product(s) was chosen so that no peak overlap occurred.

Qualitative analysis

Spiking (addition of a qualitative standard) was the main form of qualitative analysis utilizing the gas chromatograph. Prepping of samples (to be discussed) entailed the isolation of specific products using the chromatograph.

Figure 14.

Ethylation Products, and Substitute Compounds
used to Determine Chromatographic Response Factors

Product(s)	Substitute
4-pentyn-2-ol ethylation products	2-heptanol
	
4-pentyn-1-ol ethylation products	1-heptanol
	

The isolated samples were then subjected to IR and NMR investigation.

In order to prep a reaction mixture component, a sample of the mixture was injected into the selected column. As the component of interest came out the exit port, it was collected and condensed in a U-shaped glass tube which had been placed in an ice bath. One quarter inch columns were used for preparative work, as they could accommodate large (10 to 100 μliters) injections of sample, therefore reducing the number of injections required to collect a sufficient amount of the component.

Often, reaction components which differed only by a cis or trans configuration could not be separated adequately on the quarter inch columns. In these cases, the products were collected together.

Quantitative analysis

A quantitative determination of products was accomplished through the utilization of response factors. The response factor Y_x, for a given compound x relative to a given internal standard, was determined via several chromatographic analyses of a quantitative standard mixture. The relationship below shows how moles of the product x and internal standard, as well as the areas of each peak on the chromatogram define the response factor.

$$Y_x = \frac{(\text{Area of internal standard})/(\text{moles of internal standard})}{(\text{area x}) \quad / \quad (\text{moles x})}$$

Once Y_x has been calculated for a particular column, chromatograph, and temperature program, product samples containing a known amount of the internal standard could be analyzed for component x. The following relationship shows how the amount of x can be determined from analysis of chromatogram peak areas.

$$\text{moles x in reaction mixture} = \frac{(Y_x)(\text{area x})(\text{moles of internal standard})}{(\text{area of internal standard})}$$

The response factors for various materials, citing specific chromatograph, column, temperature and method of determination are presented in Table V.

Nuclear Magnetic Resonance Spectroscopy

Products of interest, which had been prepped via gas chromatographic methods were transferred to NMR tubes and diluted with carbon tetrachloride (with tetramethylsilane internal standard) to an appropriate volume for determination of the product's nuclear magnetic spectrum. The instrument used for the analysis was the Perkin Elmer Model R20B Nuclear Magnetic Resonance Spectrophotometer.

Infrared Spectroscopy

NMR samples were transferred to a sodium chloride cell and infrared spectra were determined versus a carbon tetrachloride blank (with tetramethylsilane internal standard) in a matched cell. The instrument used was the Perkin Elmer Model 457 Grating Infrared Spectrophotometer.

After samples were analyzed on IR and NMR apparatus, they were reinjected into the gas chromatograph to assure that the spectra were of pure materials.

TABLE V
CHROMATOGRAPHIC RESPONSE FACTORS FOR VARIOUS SUBSTANCES

Substance	Column (8'x1/8")	Chromatograph	Temp. (°C)	He flow rate (ml/min.)	Method *	Standard	Response Factor
n-butanol	10% XE60	F&M Model 720	100	50	D	n-heptanol	1.43
n-hexanol	10% XE60	F&M Model 720	100	50	D	n-heptanol	1.14
3-butyn-1-ol	10% XE60	F&M Model 720	100	50	D	n-heptanol	1.52
	10% Carbowax	F&M Model 720	100	50	D	n-heptanol	1.65
	10% XE60	H-P 5750	100	50	D	n-heptanol	1.54
trans-3-hexen-1-ol	10% XE60	F&M Model 720	100	50	D	n-heptanol	1.40
	10% Carbowax	F&M Model 720	100	50	D	n-heptanol	1.40
	10% XE60	H-P 5750	100	50	D	n-heptanol	1.37
other 6 carbon alkenols	10% Carbowax	F&M Model 720	100	50	A	n-heptanol	1.40
	10% XE60	H-P 5750	100	50	A	n-heptanol	1.37
4-pentyn-2-ol	10% XE60	F&M Model 720	110	50	D	n-octanol	1.48
4-pentyn-2-ol ethylated products	10% XE60	F&M Model 720	110	50	A	n-octanol	1.13
4-pentyn-1-ol	10% XE60	F&M Model 720	110	50	D	n-octanol	1.66
4-pentyn-1-ol ethylated products	10% XE60	F&M Model 720	110	50	A	n-octanol	1.07
4-phenyl-3-butyn-1-ol	10% XE60	F&M Model 720	180	50	D	n-decanol	1.53
4-phenyl-3-butyn-1-ol ethylated products	10% XE60	F&M Model 720	180	50	D	n-decanol	1.12
3-pentyn-1-ol	10% XE60	F&M Model 720	110	50	D	n-octanol	1.32
3-pentyn-1-ol ethylated products	10% XE60	F&M Model 720	110	50	A	n-octanol	1.05

* D = direct determination, A = determination by analogy

CHAPTER IV

RESULTS

Recoverability Experiments

The recoverability experiments produced the following results. N-butanol and n-hexanol were returned in the final product sample as 67% and 86%, respectively, of the original alkanes added for Reaction 1. N-butanol and n-hexanol were returned in the final product sample as 69% and 84%, respectively, of the original alkanes added for Reaction 2.

Characterization of Products

As all reactions in each group gave varying amounts of the same products, only one set of chromatograms for a single sample (viewed as characteristic) is here presented.

The XE-60 column (8'x1/8") usually provided a better separation of starting material from product(s) and was used for quantitative work. The 10% Carbowax (8'x1/8") column usually provided a better separation of products, if indeed more than one were produced, and was used when possible to determine the multiplicity and ratio of hydroalkylated products. Therefore two chromatograms are presented for each characteristic product sample of interest.

Reaction Group I. 3-Butyn-1-ol Ethylations with Diethylaluminum Chloride

The reaction conditions and yields are presented in Table VI.

The first two chromatograms are of the product sample from Reaction I-5-b. Another chromatogram of Reaction I-8-b run on 10% Carbowax shows the separation of two addition products. (See Figures 15 and 16.)

The IR and NMR of the combined deuterated products of Reaction I-10-a are presented in Figures 17 and 18. The product samples were prepped on a (2'x1/4") XE60 column.

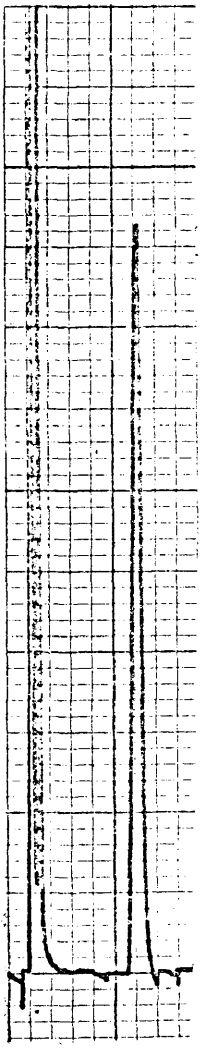
TABLE VI

RESULTS: REACTION GROUP I

ETHYLATION OF 3-BUTYN-1-OL WITH DIETHYLALUMINUM CHLORIDE

Sample	T(°C)	Time(hr)	Mole % Cp_2TiCl_2	Mole % $AlEtCl_2$	Yield of Products(%)	Return of 3-butyn-1-ol(%)	Other
I-1a	0	6	50	250	88	0	
I-1b	-78	6	50	250	0	62	
I-2a	-22	6	50	250	83	0	
I-2b	reflux	6	50	250	42	0	
I-3a	0	6	10	250	83	0	
I-3b	0	6	25	250	76	0	
I-4a	0	6	10	250	93	0	
I-4b	0	6	25	250	80	0	
I-5a	0	0.25 after addn	10	250	54	34	
I-5b	0	0.25 after addn	10	250	64	17	
I-6a	0	6	10	100	8	44	
I-6b	0	6	10	100	7	34	
I-7a	0	6	10	175	79	0	
I-7b	0	6	10	175	75	0	
I-8a	0	4	10	250	83	0	
I-8b	0	4	10	250	66	0	
I-9a	0	6	10	250	78	0	Benzene solvent
I-9b	0	6	10	250	82	0	Benzene solvent
I-10a	0	2	10	250	82	0	Hydrolysis with deuterated water
I-10b	0	2	10	250	99	0	Hydrolysis with deuterated water
I-11a	25	6.3	-	250	5	62	25 mole % Cp_2ZrCl_2
I-11b	25	6.3	-	250	7	69	25 mole % Cp_2ZrCl_2

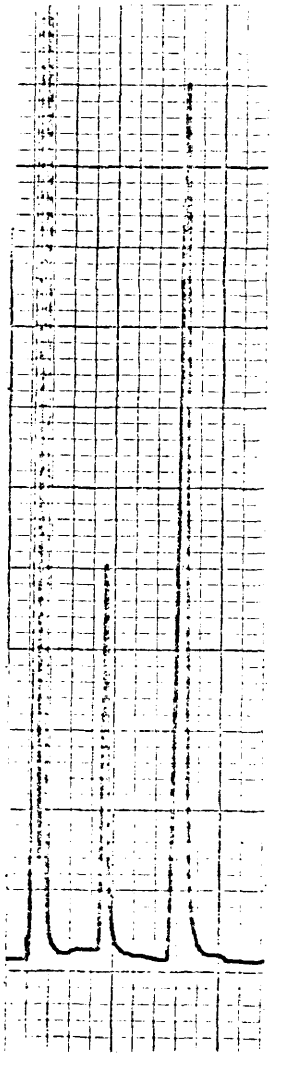
Figure 15.
Results: Reaction Group I
Chromatograms of 3-Butyn-1-ol Ethylation
Reaction Samples



a

10% Carbowax

a) Combination of 3-butyn-1-ol and 3-butyn-1-ol ethylated products



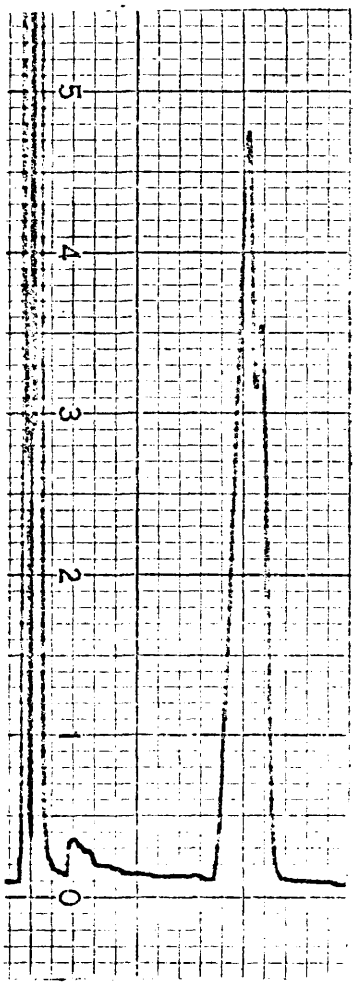
b c

10% XE 60

b) 3-butyn-1-ol

c) 3-butyn-1-ol ethylated products

Figure 16.
Results: Reaction Group I
Chromatogram Showing
Separation of 3-Butyn-1-ol Ethylation Products
on 10% Carbowax Column



a

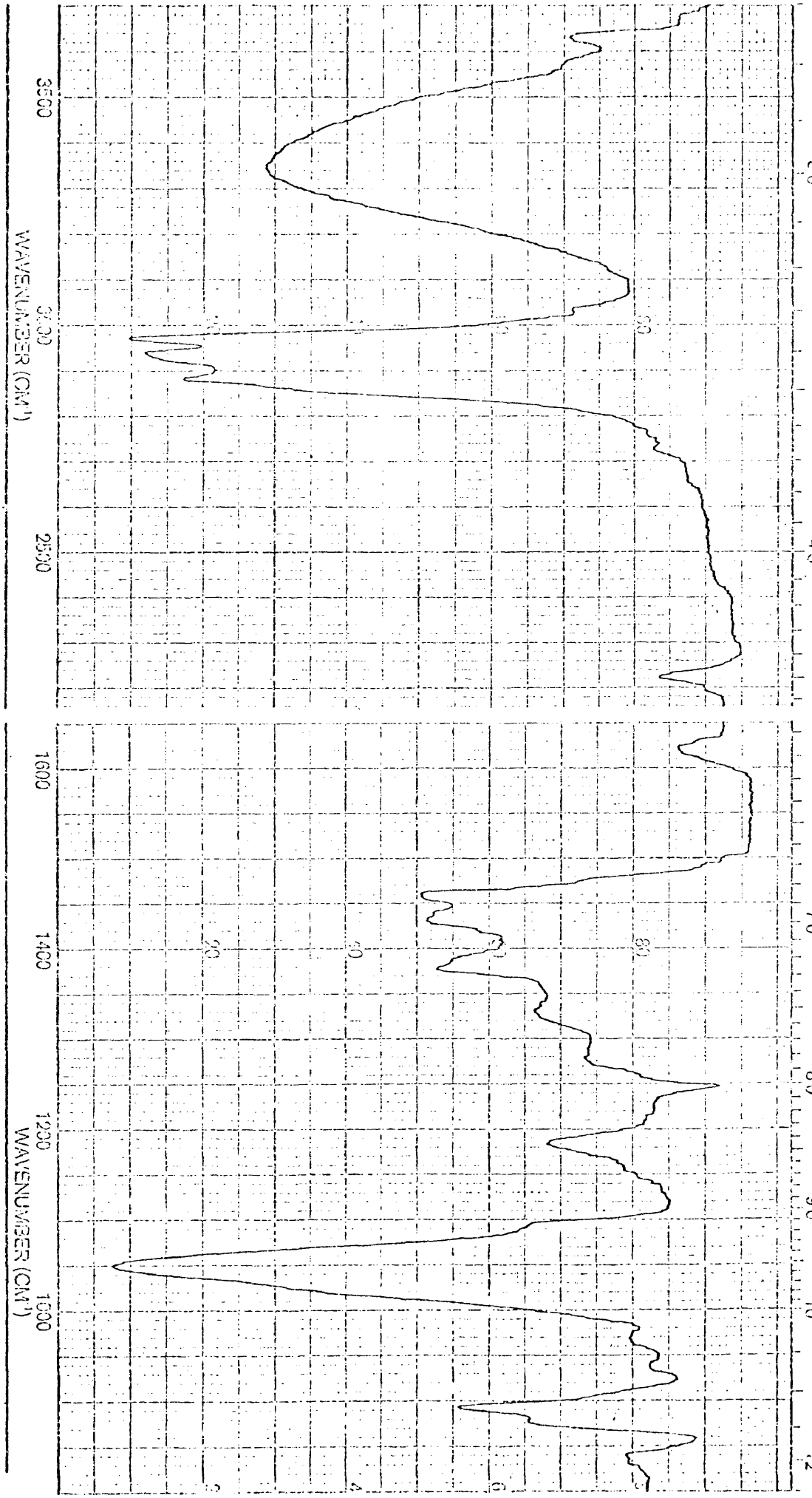
a) 3-butyn-1-ol ethylation products

Figure 17

Results: Reaction Group I

IR of Combined 3-Butyn-1-ol

Ethylation Products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2500
WAVENUMBER (CM⁻¹)
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4.0
1600
1400
1200
1000
WAVENUMBER (CM⁻¹)
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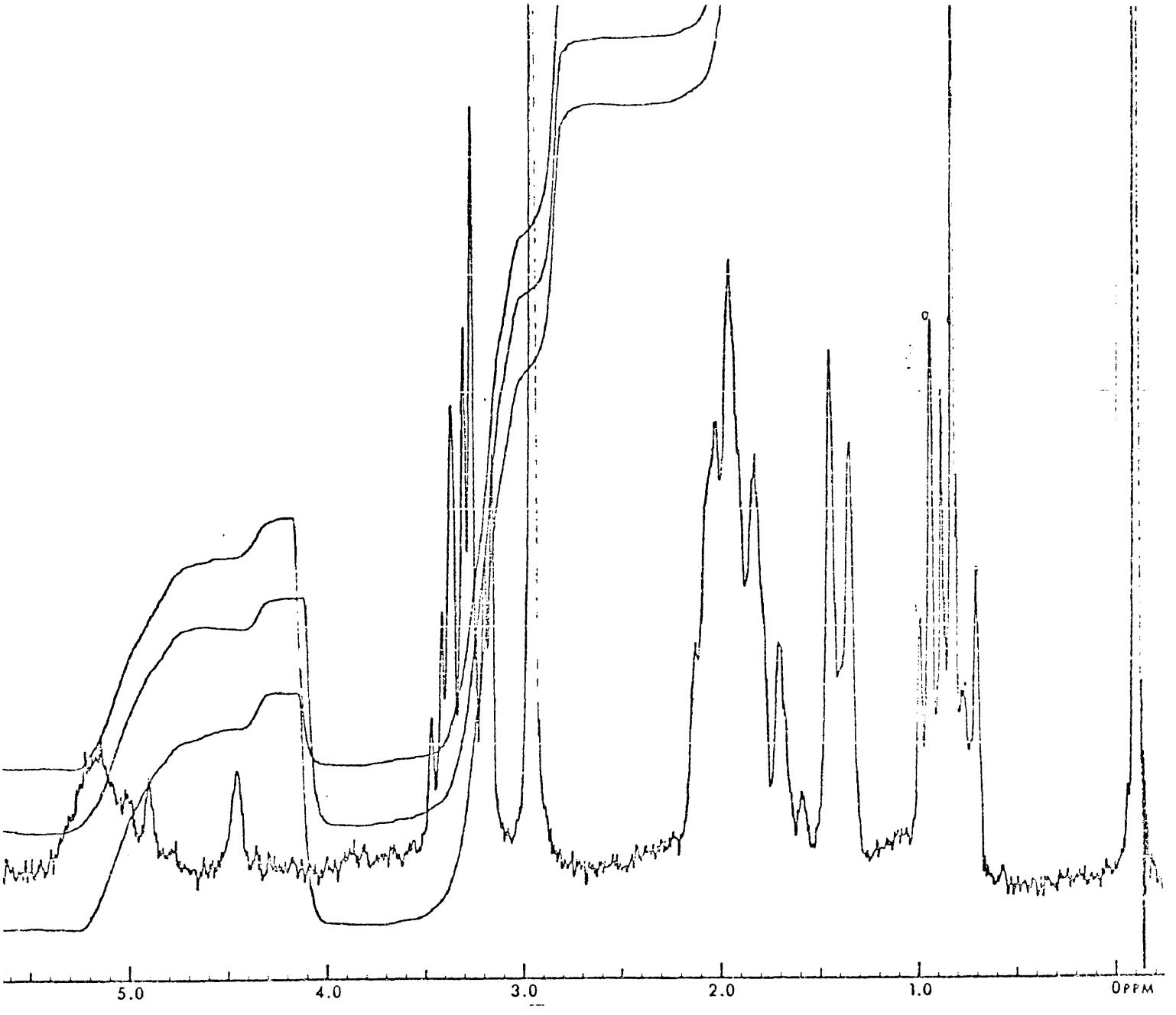
8.0
9.0
10
12

Figure 18.
Results: Reaction Group I
NMR of Combined 3-Butyn-1-ol
Ethylation Products



Reaction Group II. Ethylation of 4-Pentyn-2-ol with Diethylaluminum Chloride

The reaction conditions, and quantitative yields of the 4-pentyn-2-ol ehtylations are presented in Table VII.

The characteristic chromatograms (Figure 19) are of the product sample from Reaction II-1-b.

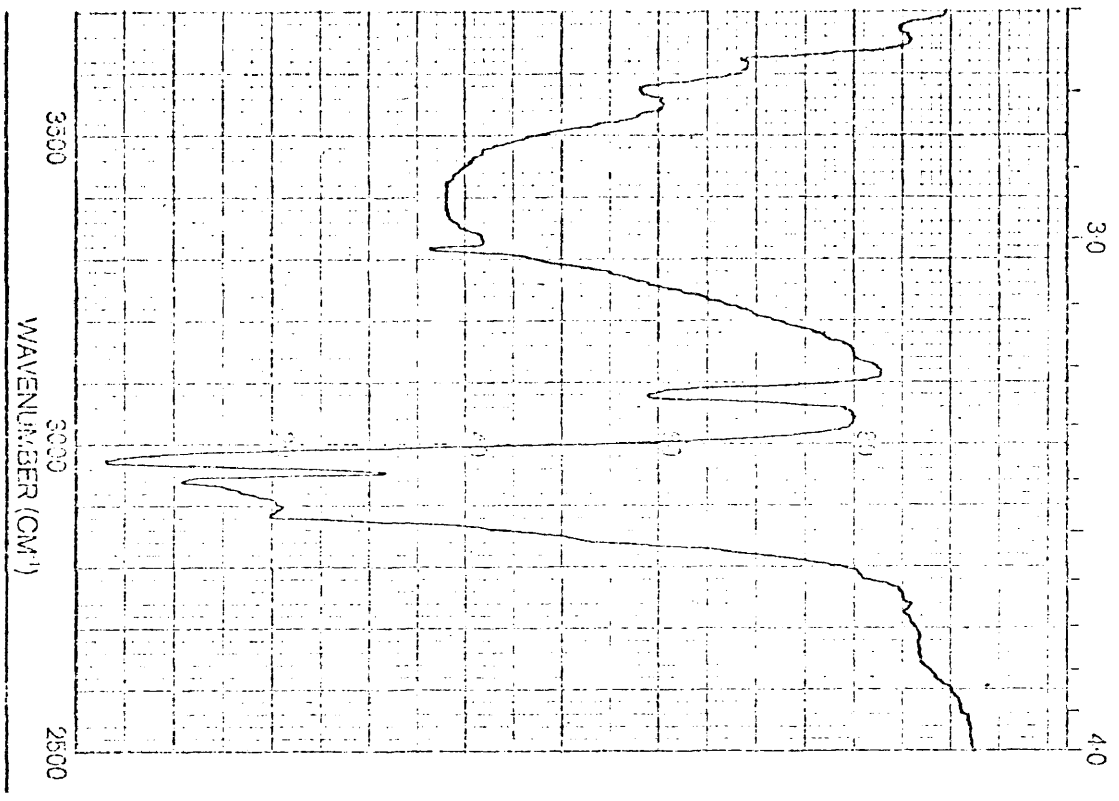
The IR and NMR of two separate products from Reaction II-1-a are presented in Figures 20 through 22. Figures 24 and 25 are IR and NMR of the combined products. The samples were prepped on a (6'x1/4") 10% Carbowax column.

TABLE VII

RESULTS: REACTION GROUP II

ETHYLATION OF 4-PENTYN-2-OL WITH DIETHYLALUMINUM CHLORIDE

Sample	T(°C)	Time(hr)	Mole % Cp_2TiCl_2	Mole % $AlEt_2Cl$	Yield of Products(%)	Return of 4-pentyn-2-ol
II-1a	0	4	10	250	not determined	not determined
II-1b	0	4	10	250	52	4
II-2a	-35	4.3	10	250	8	60
II-2b	-35	4.3	10	250	8	64
II-3a	25	4	10	250	33	4
II-3b	25	4	10	250	30	6
II-4a	0	4	50	250	66	1
II-4b	0	4	50	250	59	2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2500
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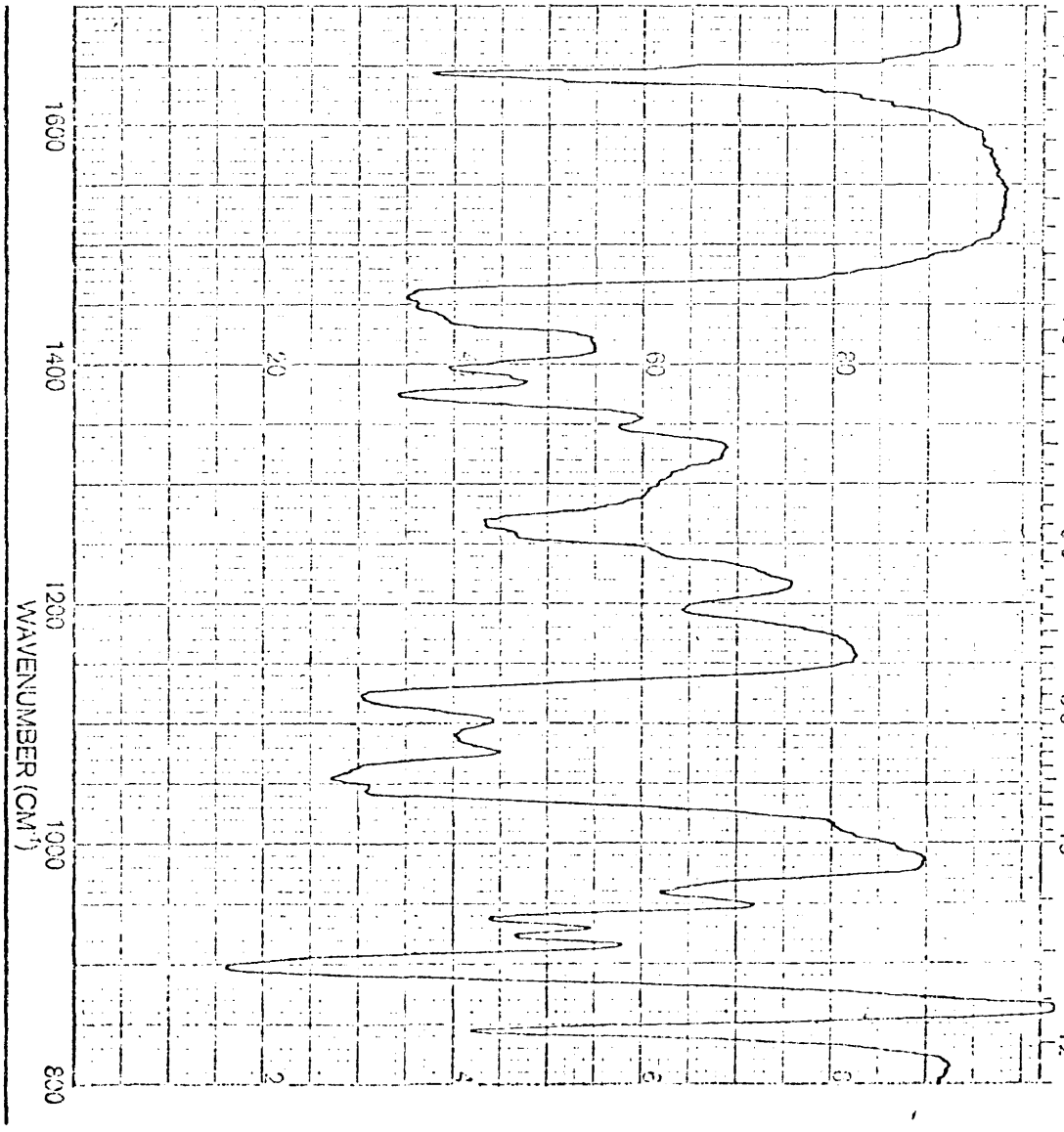
4.0


1600
1400
1200
1000
800
WAVENUMBER (CM⁻¹)
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7.0
8.0
9.0
10
12

Figure 21.
Results: Reaction Group II
NMR of 4-Pentyn-2-ol
Ethylation Product I

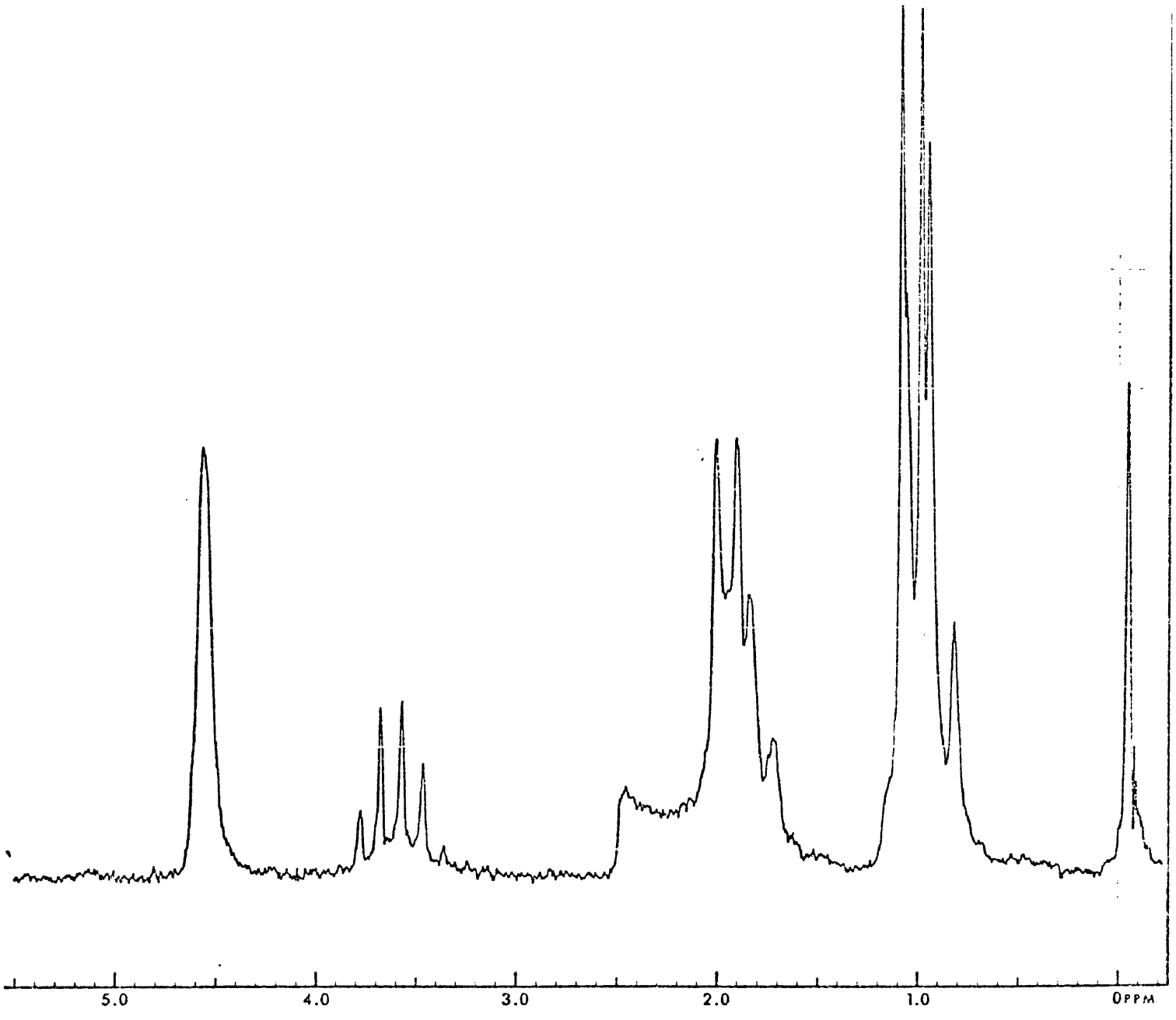
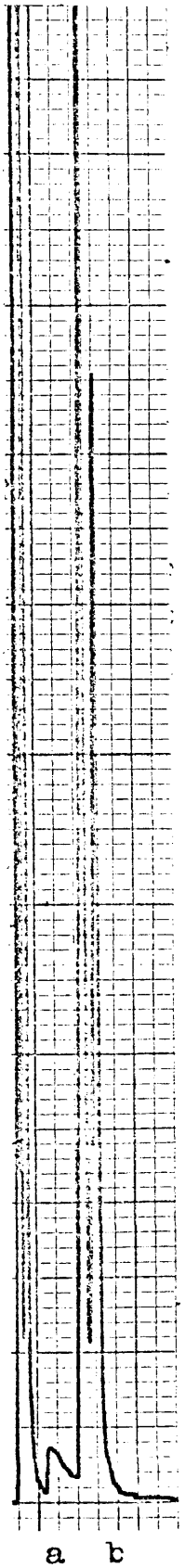
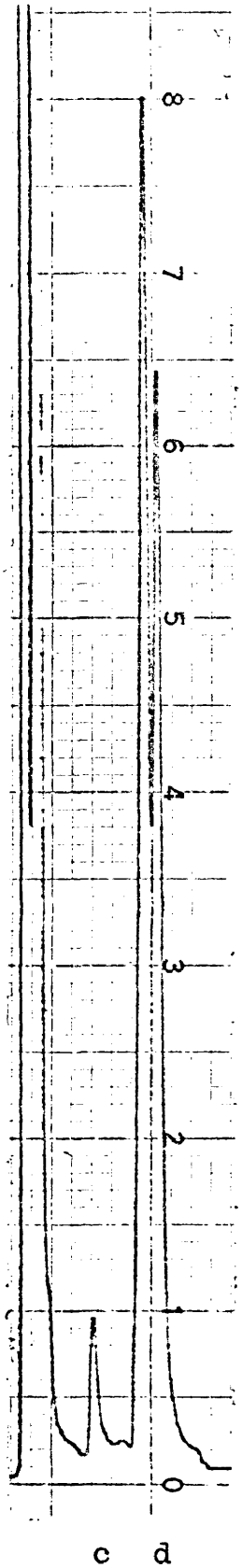


Figure 19.
Results: Reaction Group II
Chromatograms of 4-Pentyn-2-ol
Ethylation Reaction Samples



10% Carbowax
a) 4-pentyn-2-ol
b) 4-pentyn-2-ol
ethylated products



10% XE60
c) 4-pentyn-2-ol
d) 4-pentyn-2-ol
ethylated products

Figure 20.

Results: Reaction Group II

IR of 4-Pentyn-2-ol

Ethylation Product I

Figure 23.
Results: Reaction Group II
NMR of 4-Pentyn-2-ol
Ethylation Product II

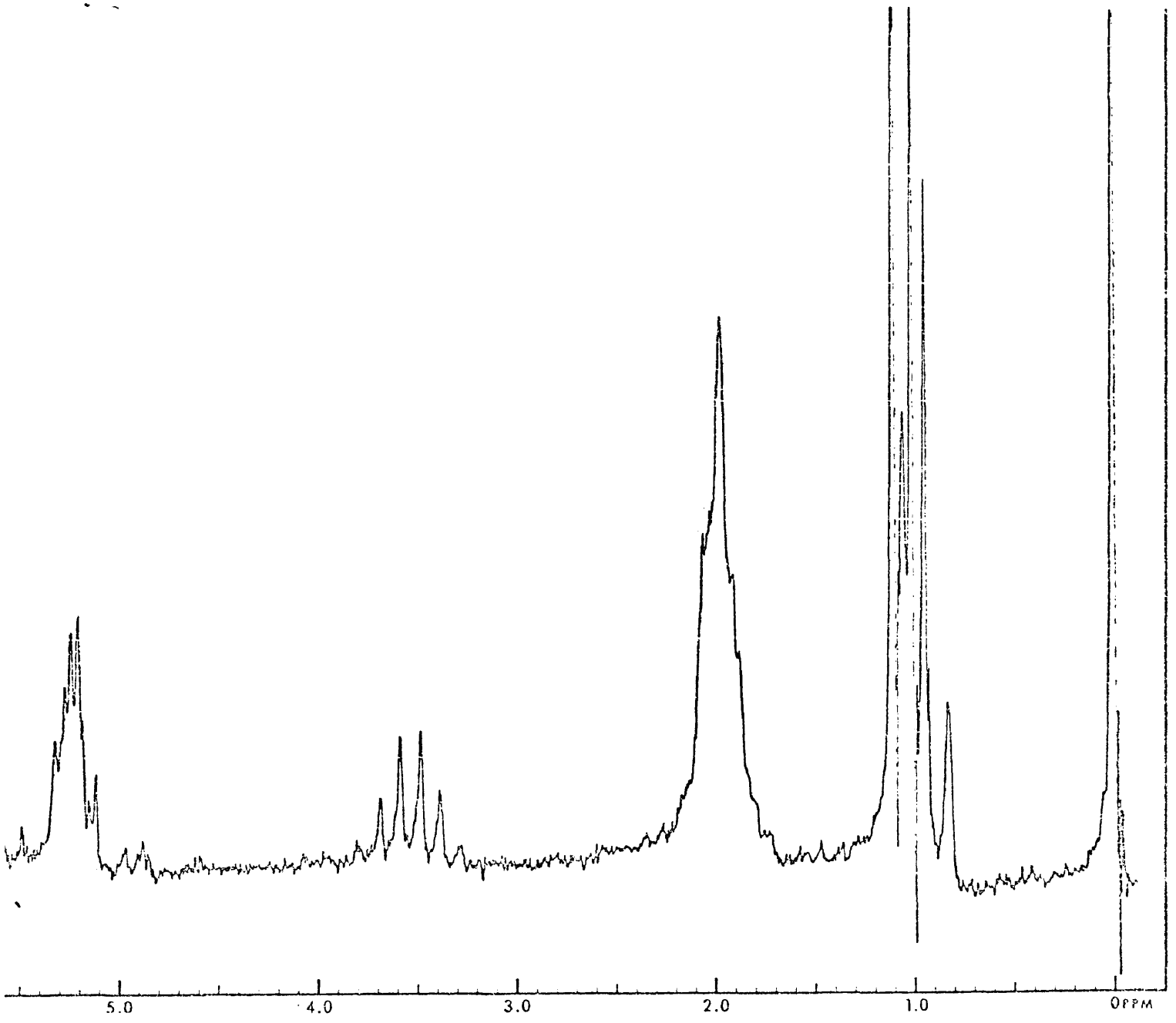
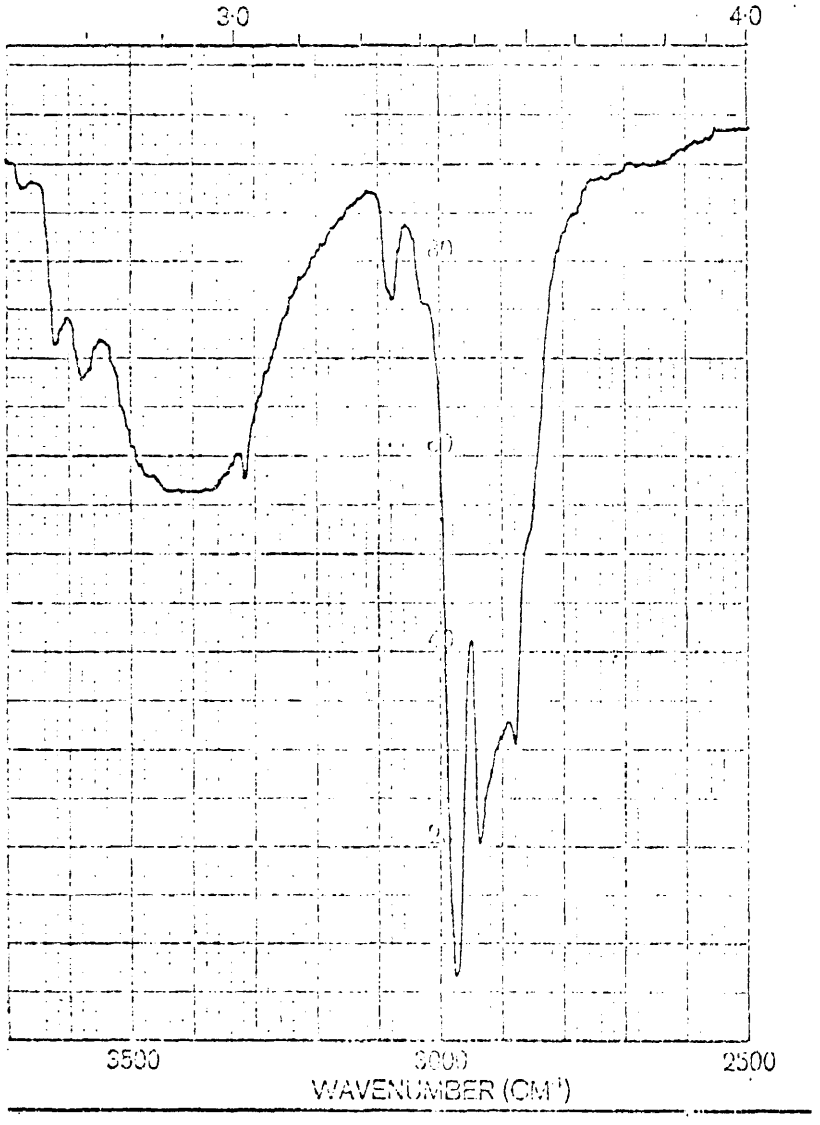


Figure 24.

Results: Reaction Group II

IR of Combined 4-Pentyn-2-ol

Ethylation Products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4·0
3500
2500
WAVENUMBER (CM⁻¹)

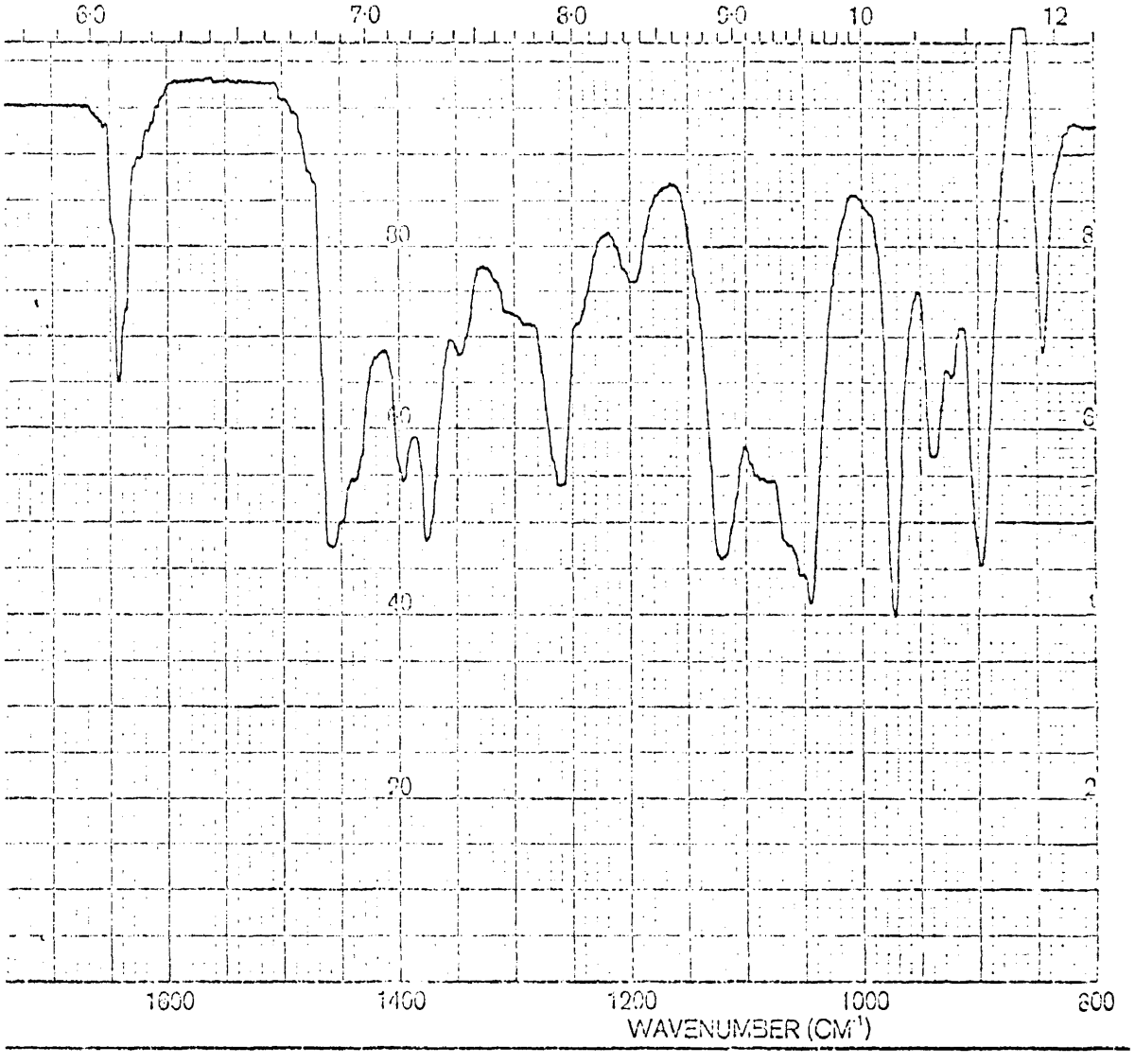
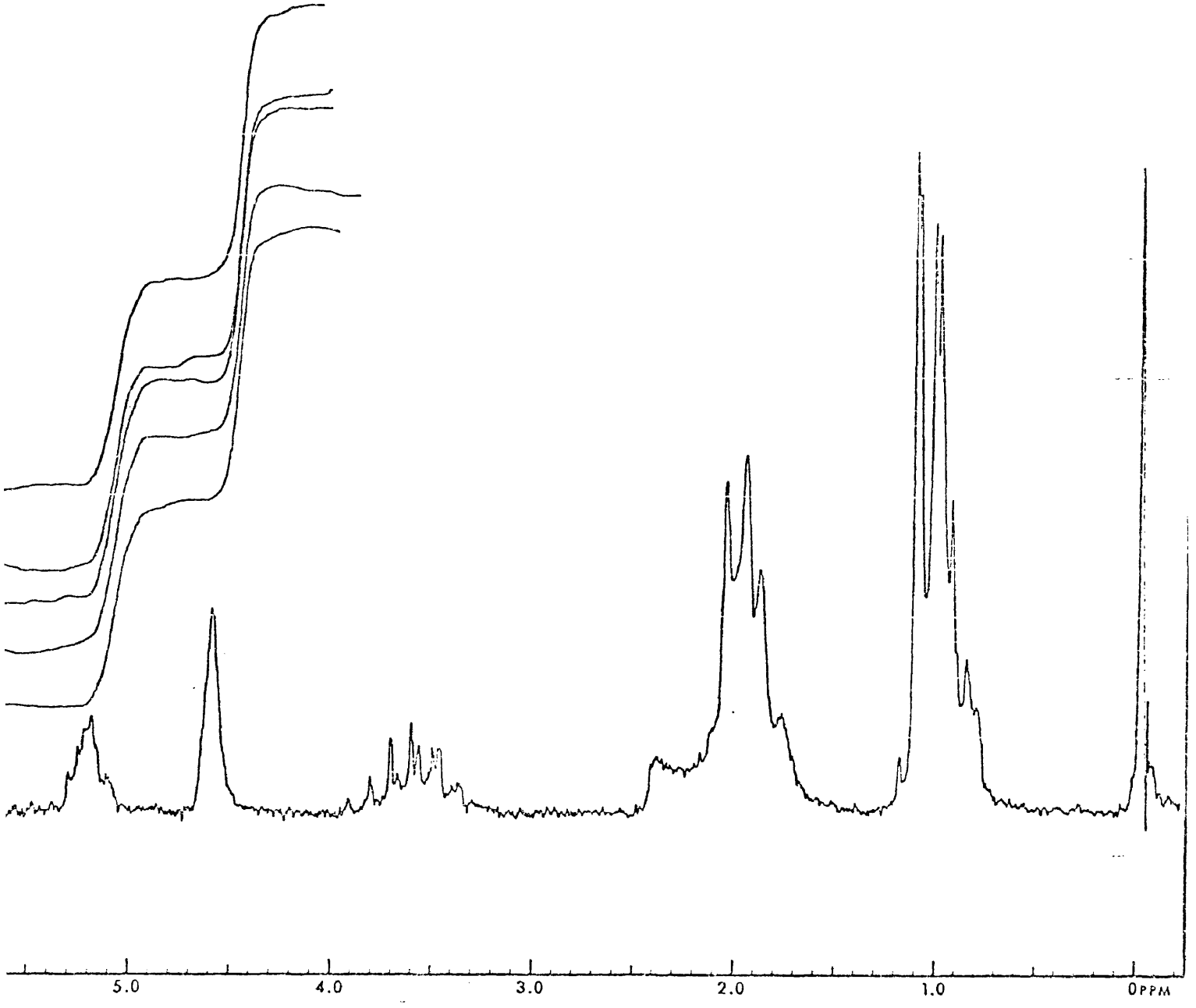

6·0
7·0
8·0
9·0
10
12
1600
1400
1200
1000
800
WAVENUMBER (CM⁻¹)

Figure 25.
Results: Reaction Group II
NMR of Combined 4-Pentyn-2-ol
Ethylation Products



Reaction Group III. Ethylation of 4-Pentyn-1-ol with Diethylaluminum Chloride

The reaction conditions and yields of the 4-pentyn-1-ol ethylations are presented in Table VIII.

The characteristic chromatograms (Figure 26) are of the product sample III-1-a.

IR and NMR of combined products from Reaction III-2-b are presented in Figures 27 and 28. The samples were prepped on a (6'x1/4") 10% Carbowax column.

TABLE VIII

RESULTS: REACTION GROUP III

ETHYLATION OF 4-PENTYN-1-OL WITH DIETHYLALUMINUM CHLORIDE

Sample	T(°C)	Time(hr)	Mole % Cp_2TiCl_2	Mole % $AlEt_2Cl$	Yield of Products(%)	Return of 4-pentyn-1-ol
III-1	0	4	10	250	48	11
III-2a	0	4	50	250	68	0
III-2b	0	4	50	250	74	0

Figure 26.
Results: Reaction Group III
Chromatograms of 4-Pentyn-1-ol
Ethylation Reaction Samples

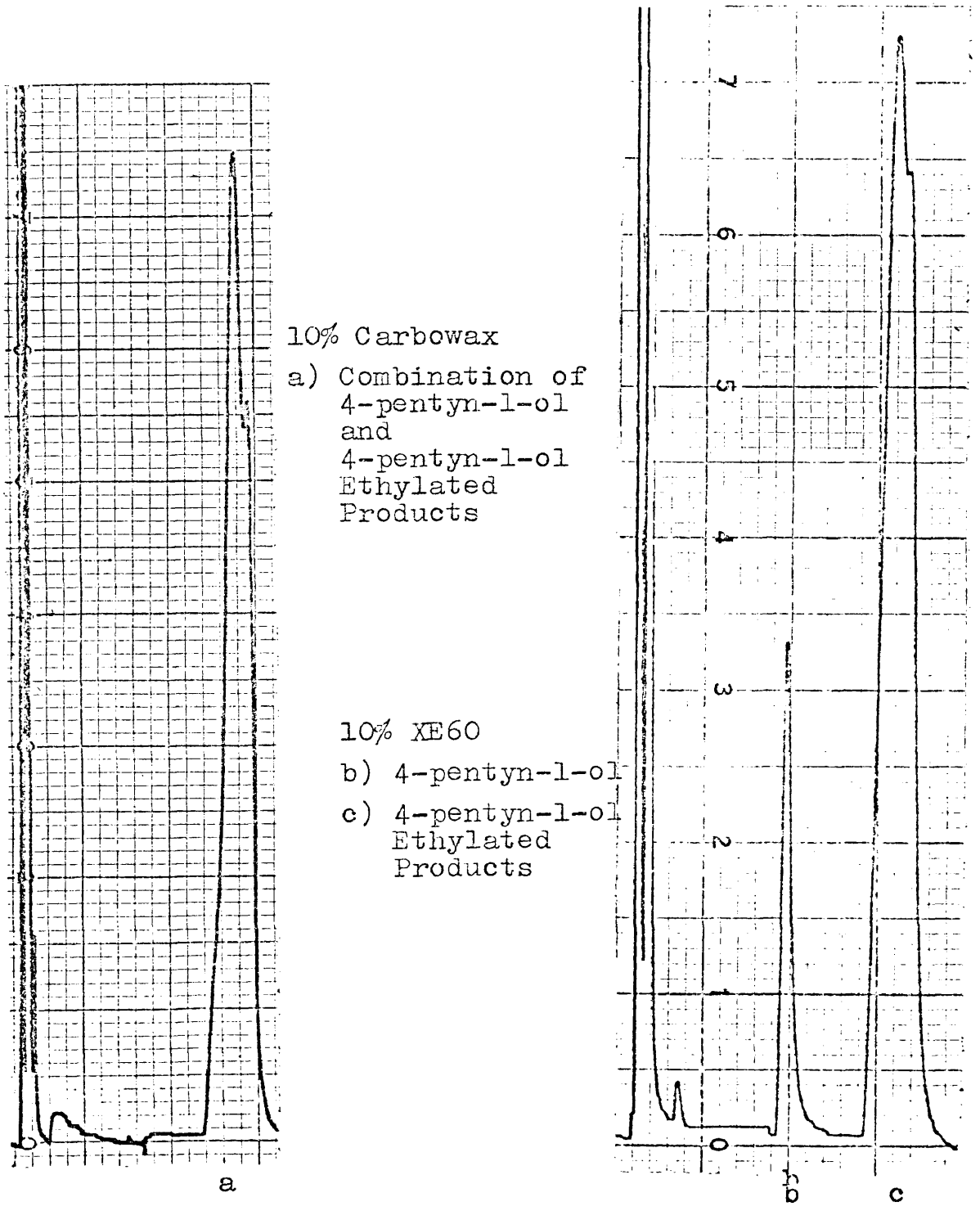
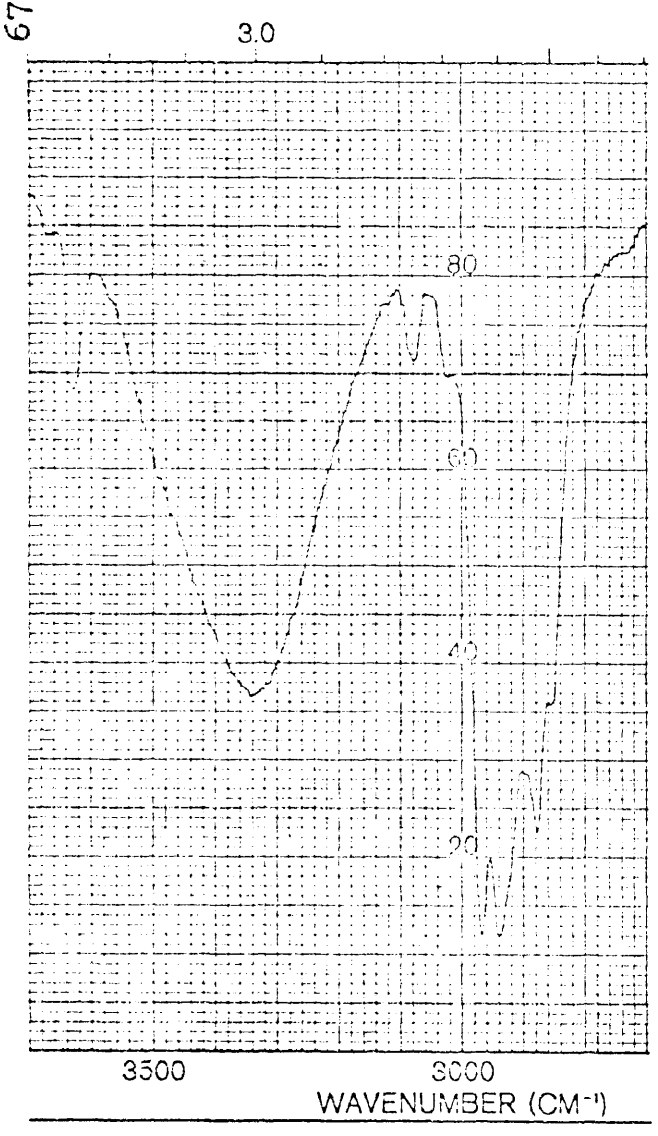


Figure 27.

Results: Reaction Group III

IR of Combined 4-Pentyn-1-ol

Ethylation Products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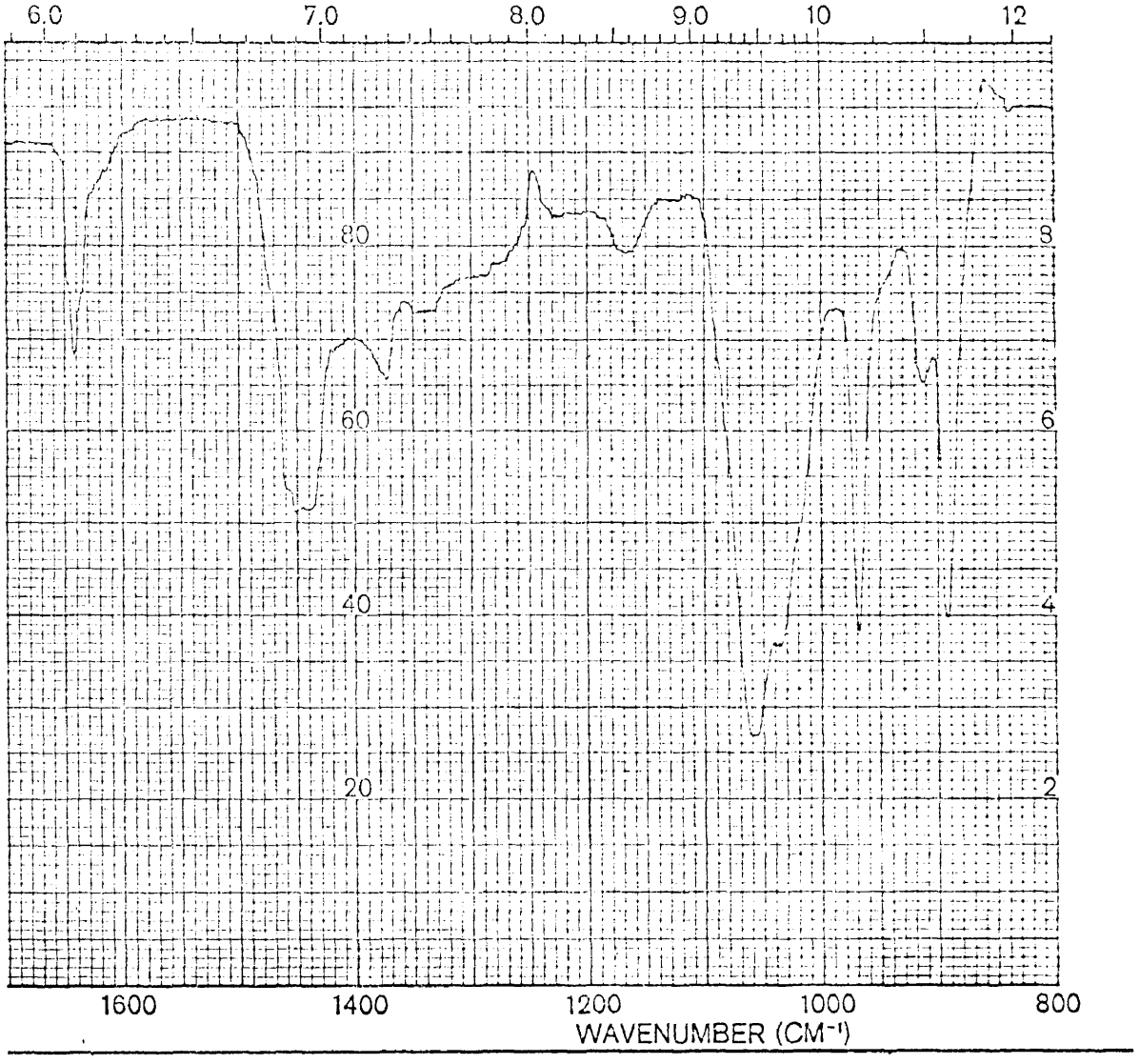
40
20
3500
3000
WAVENUMBER (CM⁻¹)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7.0
8.0
9.0
10
12
80
60
40
20
8
6
4
2
1600
1400
1200
1000
800
WAVENUMBER (CM⁻¹)

Reaction Group IV. Ethylation of 3-Pentyn-1-ol with Diethylaluminum Chloride

The reaction conditions and yields of the 3-pentyn-1-ol ethylations are presented in Table IX.

The characteristic chromatograms (Figure 29) are of the product sample IV-3-a.

IR and NMR of the product from Reaction IV-3-b are presented in Figures 30 and 31. The samples were prepped on a (6'x1/4") 10% Carbowax column.

TABLE IX

RESULTS: REACTION GROUP IV

ETHYLATION OF 3-PENTYN-1-OL WITH DIETHYLALUMINUM CHLORIDE

Sample	T(°C)	Time(hr)	Mole % Cp_2TiCl_2	Mole % $AlEt_2Cl_2$	Yield of Products(%)	Return of 3-pentyn-1-ol
IV-1a	0	4	10	250	very small	large
IV-1b	0	4	10	250	very small	large
IV-2a	0	4	25	250	12	35
IV-2b	0	4	25	250	17	45
IV-3a	0	4	50	250	46	21
IV-3b	0	4	50	250	46	26

Figure 28.

Results: Reaction Group III

NMR of Combined 4-Pentyn-1-ol

Ethylation Products

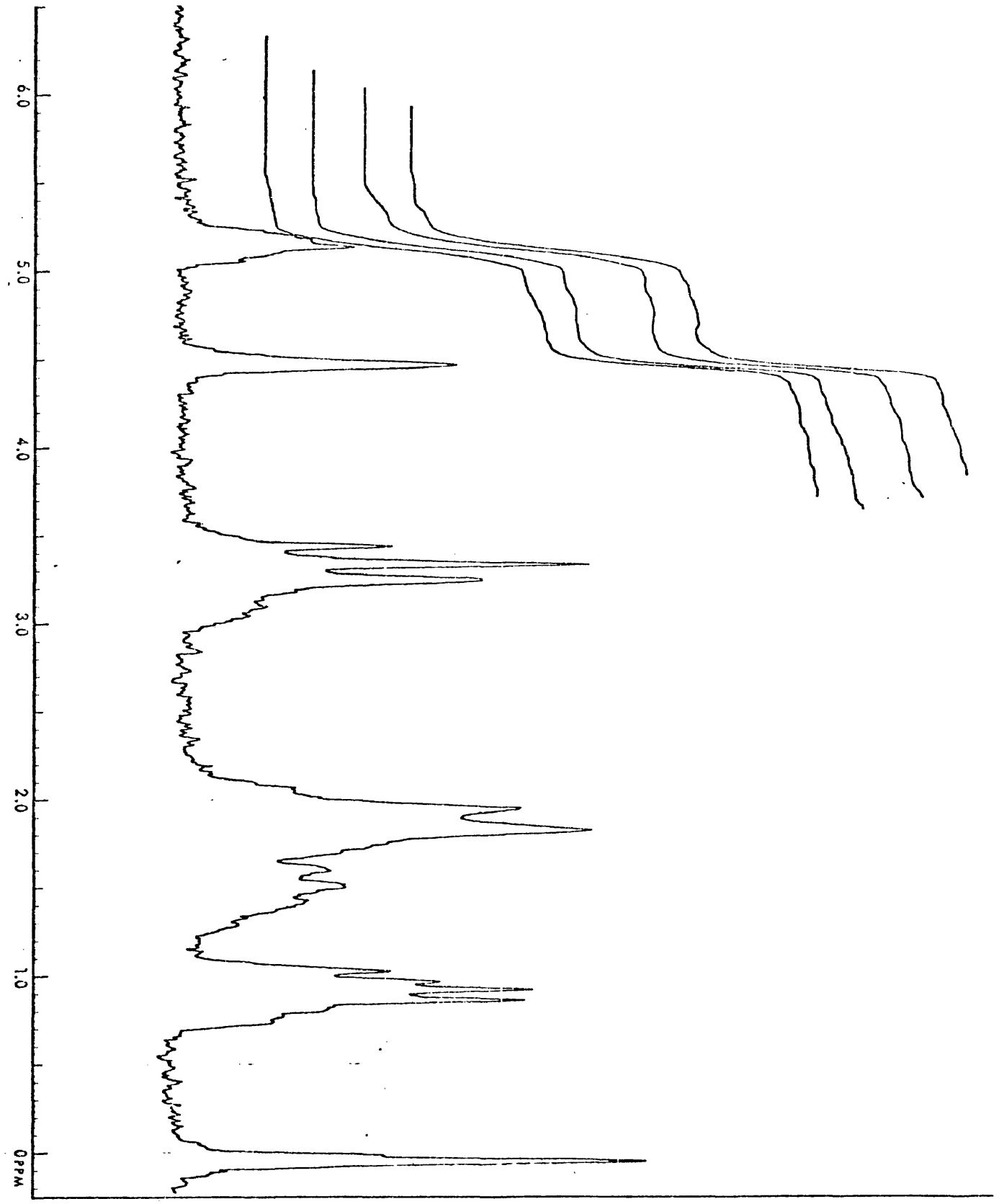
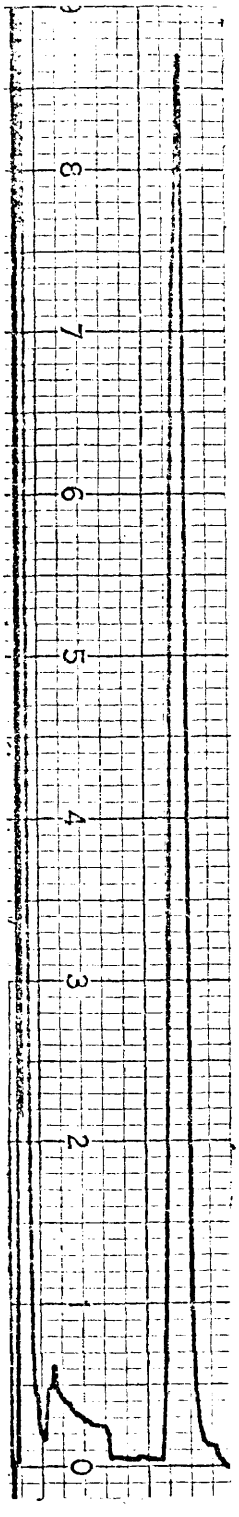

6.0
5.0
4.0
3.0
2.0
1.0
0PPM

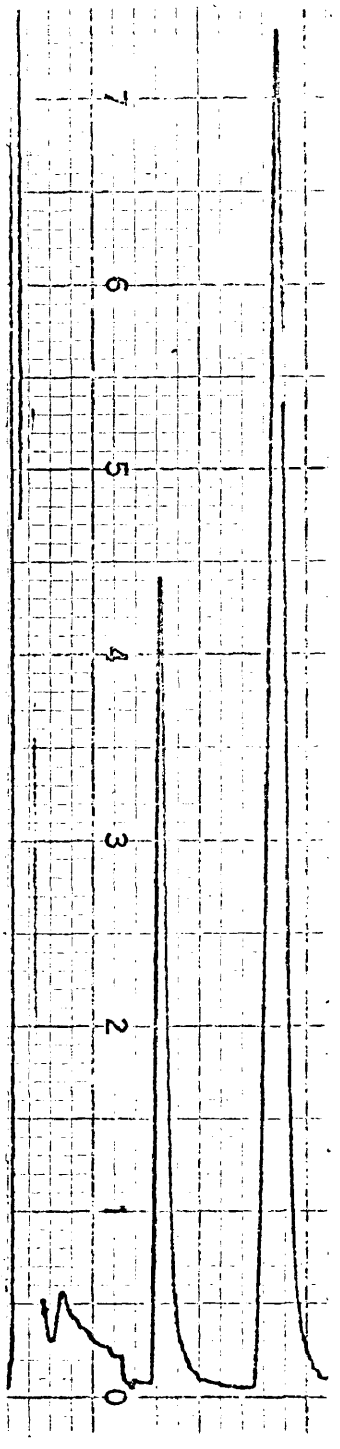
Figure 29.
Results: Reaction Group IV
Chromatograms of 3-Pentyn-1-ol
Ethylation Reaction Samples



a

10% Carbowax

a) Combined 3-pentyn-1-ol and 3-pentyn-1-ol Ethylated Products



b c

10% XE60

b) 3-pentyn-1-ol

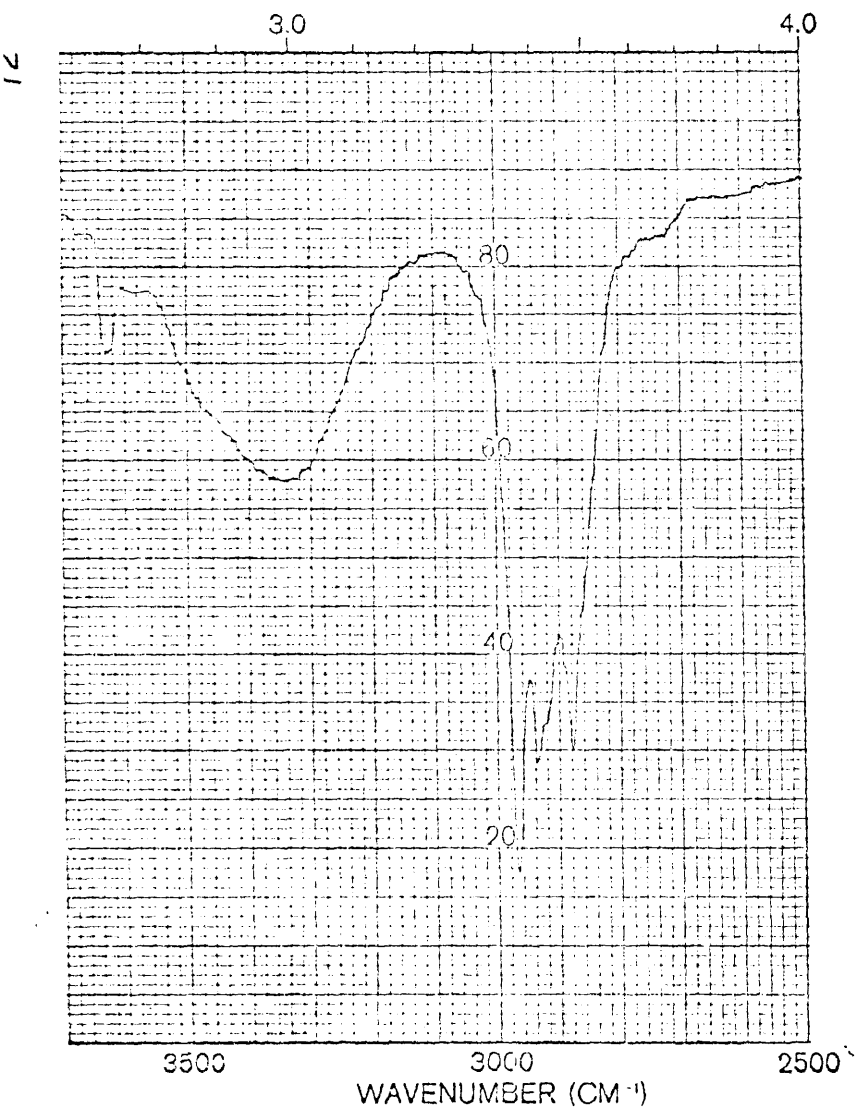
c) 3-pentyn-1-ol Ethylated Product

Figure 30.

Results: Reaction Group IV

IR of 3-Pentyn-1-ol

Ethylation Product


3.0
4.0
80
60
40
20
3500
3000
2500
WAVENUMBER (CM⁻¹)

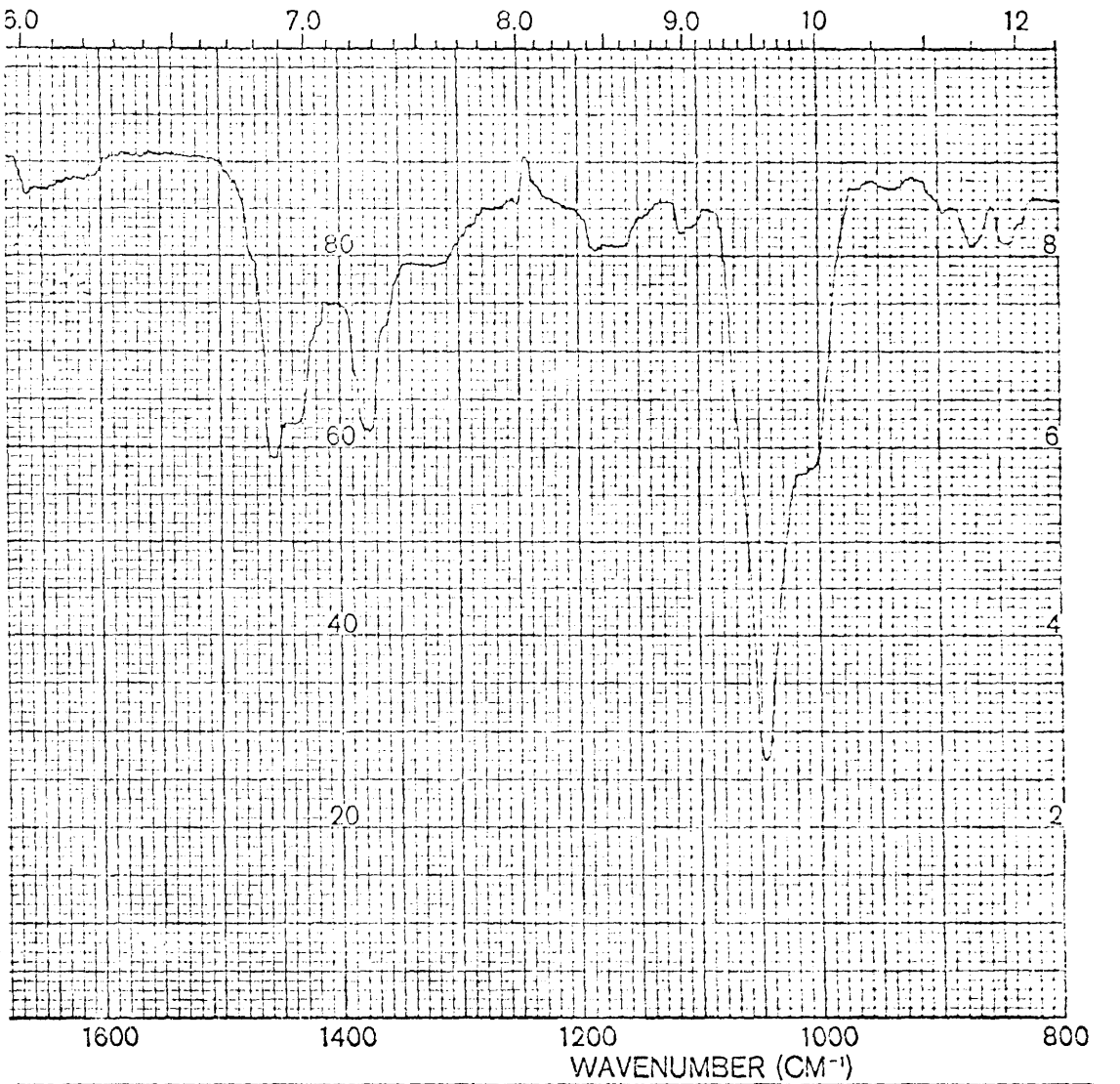
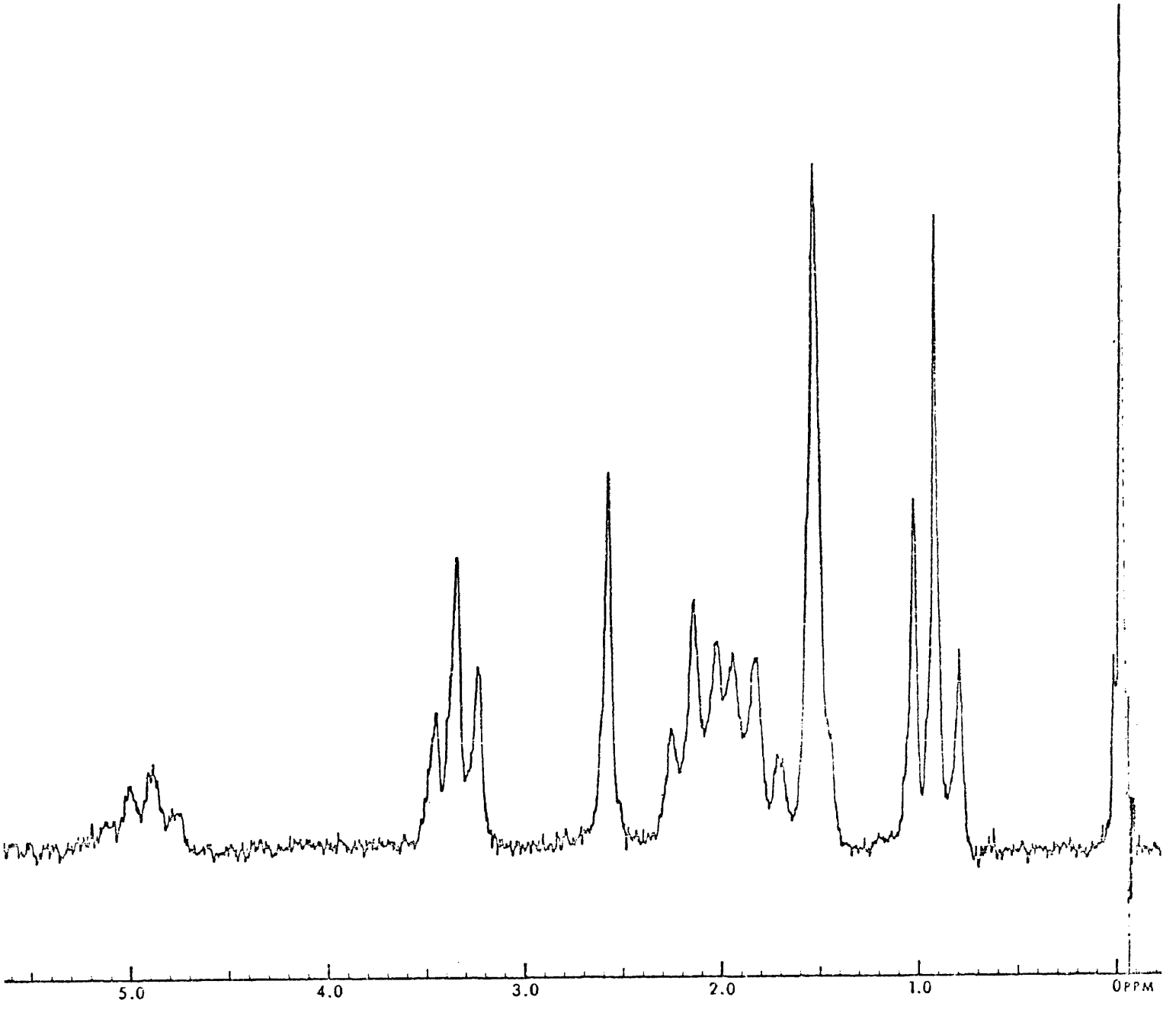

5.0
7.0
8.0
9.0
10
12
80
60
40
20
8
6
4
2
1600
1400
1200
1000
800
WAVENUMBER (CM⁻¹)

Figure 31.
Results: Reaction Group IV
NMR of 3-Pentyn-1-ol
Ethylation Reaction Product



Reaction Group V. Ethylation of 4-Phenyl-3-Butyn-1-ol with Diethylaluminum Chloride

The reaction conditions and yields of the 4-phenyl-3-butyn-1-ol ethylations are presented in Table X.

The characteristic chromatograms (Figure 32) are from the product sample V-2-a.

IR and NMR of the product from Reaction V-2-b are presented in Figures 33 and 34. The samples were prepped on a (6'x1/4") 10% Carbowax column.

TABLE X

RESULTS: REACTION GROUP V

ETHYLATION OF 4-PHENYL-3-BUTYN-1-OL WITH DIETHYLALUMINUM CHLORIDE

Sample	T(°C)	Time(hr)	Mole % Cp_2TiCl_2	Mole % $AlEt_2Cl$	Yield of Products(%)	Return of 4-phenyl-3-butyn-1-ol
V-1a	0, then 25	6, 10.5	20	250	14	58
V-1b	0, then 25	6, 10.5	20	250	14	51
V-2a	0	4	50	250	43	34
V-2b	0	4	50	250	41	41

Figure 32.

Results: Reaction Group V

Chromatograms of 4-Phenyl-3-Butyn-1-ol

Ethylation Reaction Samples

a) n-decanol standard

b) 4-phenyl-3-butyn-1-ol Ethylated Product

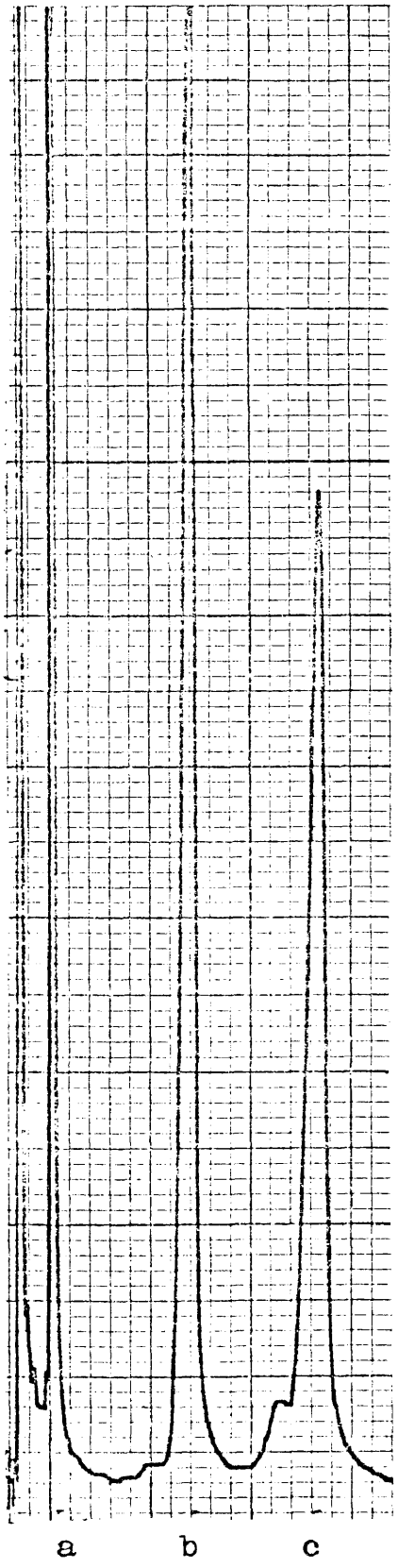
c) 4-phenyl-3-butyn-1-ol

d) n-decanol standard

e) 4-phenyl-3-butyn-1-ol Ethylated Product

f) 4-phenyl-3-butyn-1-ol

10% Carbowax



10% XE60

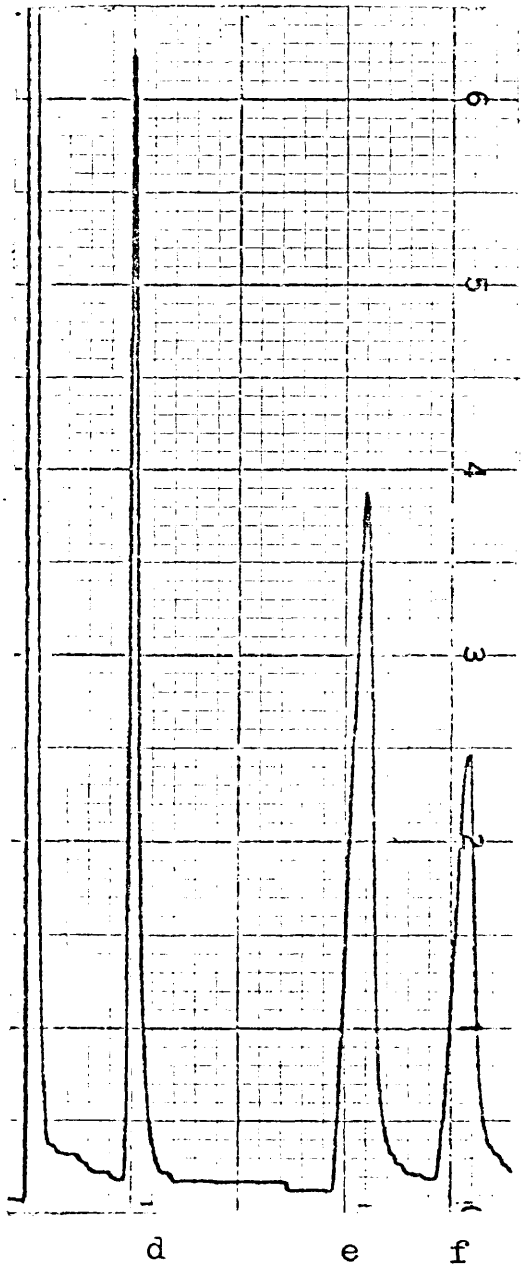


Figure 33.

Results: Reaction Group V

IR of 4-Phenyl-3-Butyn-1-ol

Ethylation Product

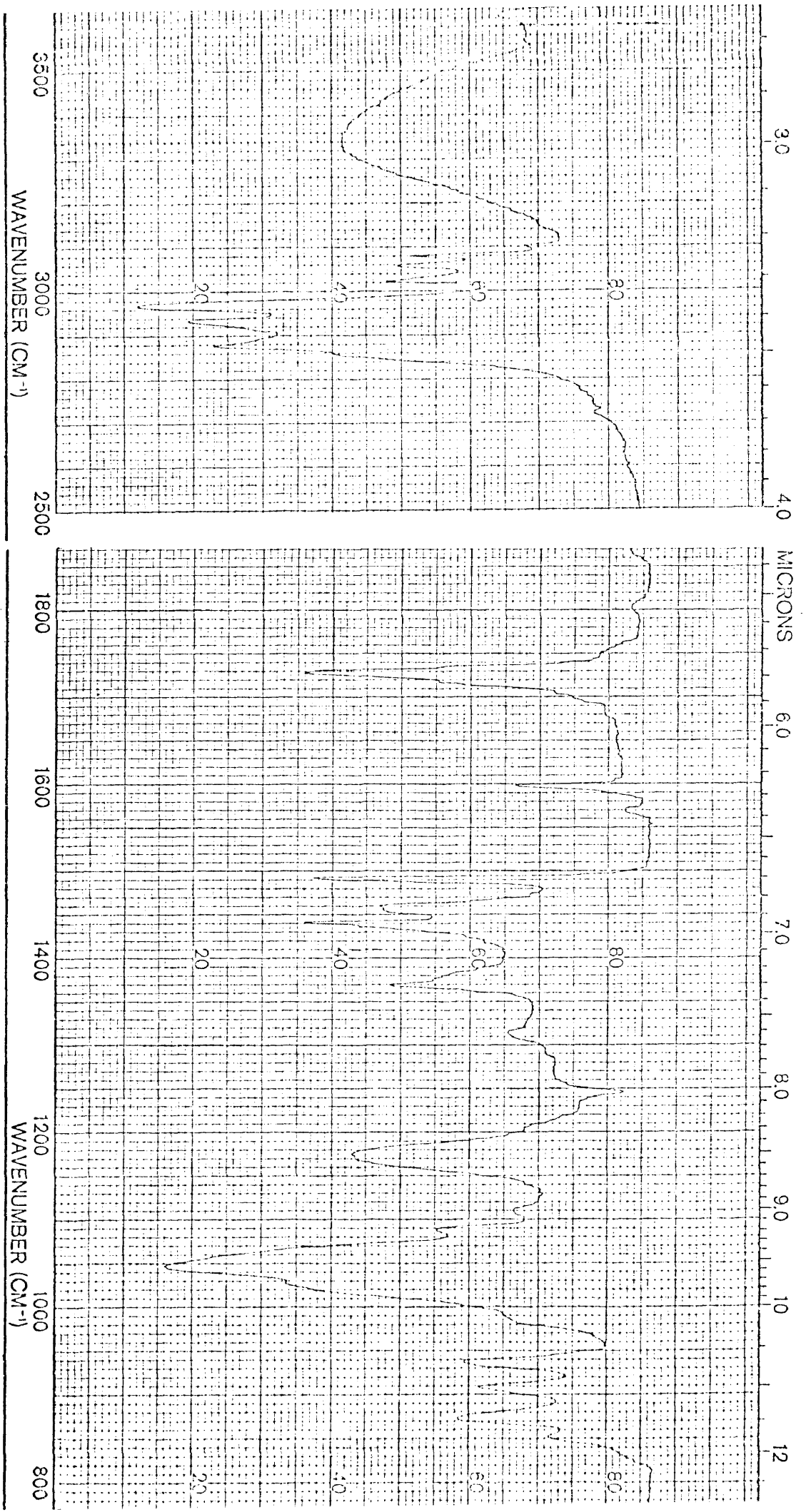
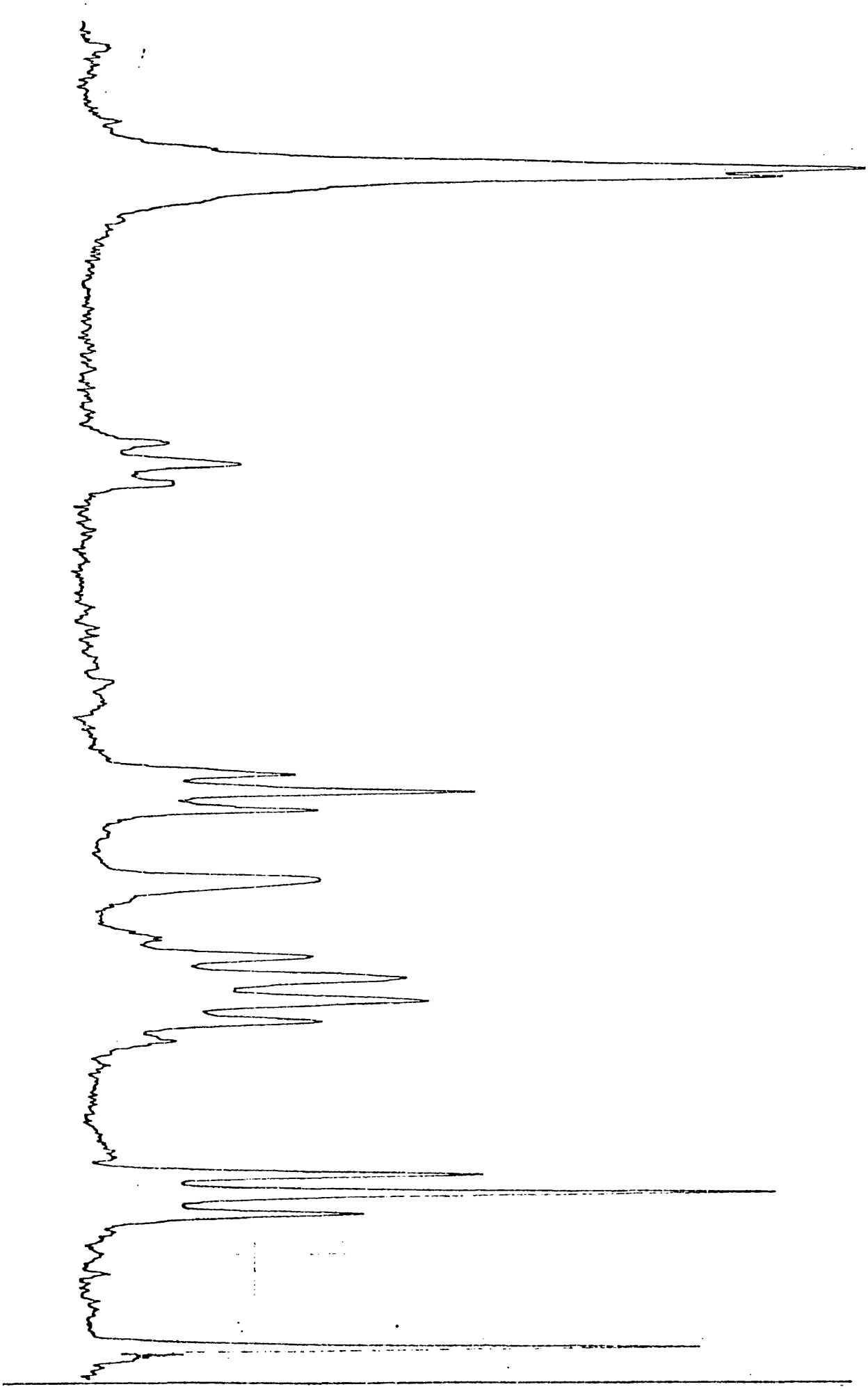

3500
3000
2500
WAVENUMBER (CM⁻¹)
3.0
4.0
MICRONS
6.0
7.0
8.0
9.0
10
12
1800
1600
1400
1200
1000
800
WAVENUMBER (CM⁻¹)

Figure 34.

Results: Reaction Group V

NMR of 4-Phenyl-3-Butyn-1-ol

Ethylation Product



Reaction Group VI. Ethylation of 2-Propyn-1-ol with Diethylaluminum Chloride

The reaction conditions and yields are presented in Table XI.

The characteristic chromatograms (Figure 35) are from the product sample VI-1-a.

IR and NMR were not run.

TABLE XI

RESULTS: REACTION GROUP VI

ETHYLATION OF 2-PROPYN-1-OL WITH DIETHYLALUMINUM CHLORIDE

Sample	T(°C)	Time(hr)	Mole % Cp_2TiCl_2	Mole % $AlEt_2Cl_2$	Yield of Products(%)	Return of 2-propyn-1-ol
VI-1a	0	4	10	250	small	large
VI-1b	0	4	10	250	small	large

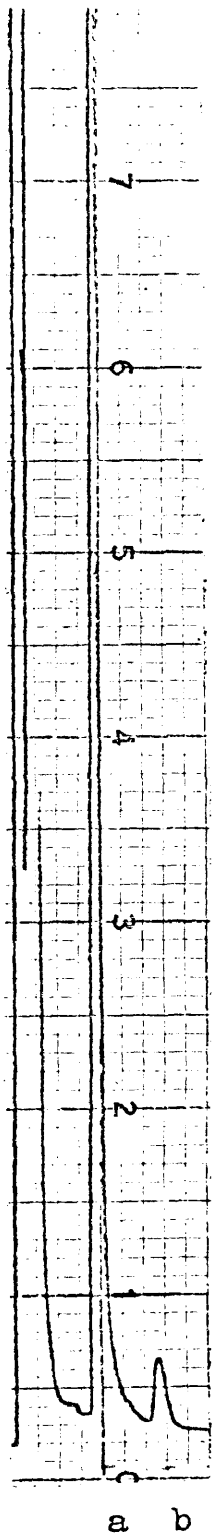
Figure 35.

Results: Reaction Group VI

Chromatograms of 2-Propyn-1-ol

Ethylation Reaction Samples

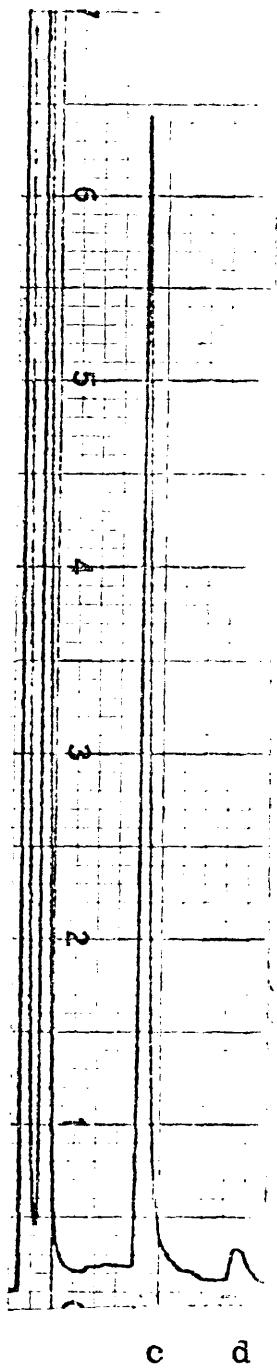
10% Carbowax



a) 2-propyn-1-ol
b) 2-propyn-1-ol Ethylated Product

a b

10% XE 60



c) 2-propyn-1-ol
d) 2-propyn-1-ol Ethylated Product

c d

Reaction Group VII. Ethylation of 5-Hexyn-1-ol with Diethylaluminum Chloride

The reaction conditions and yields are presented in Table XII.

The characteristic chromatograms (Figure 36[a]) are from the product sample VII-1-a.

IR and NMR were not run.

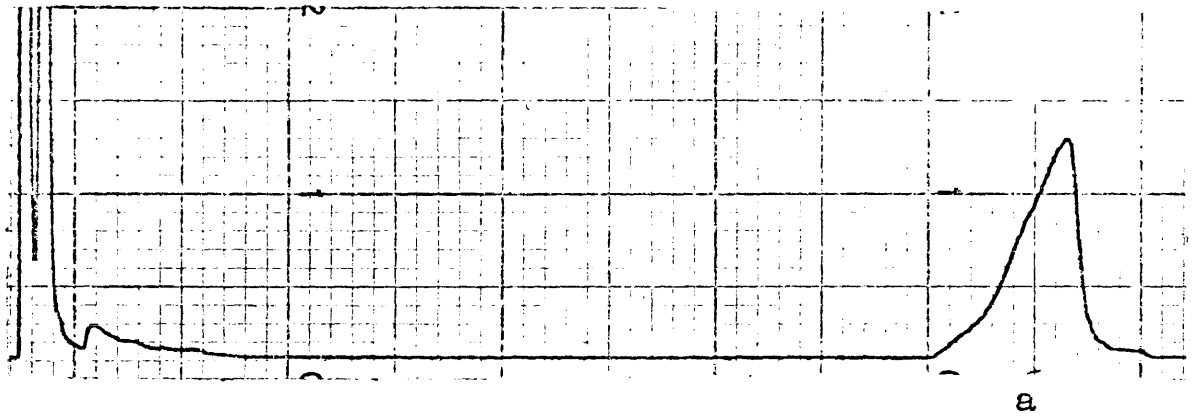
TABLE XII

RESULTS: REACTION GROUP VII

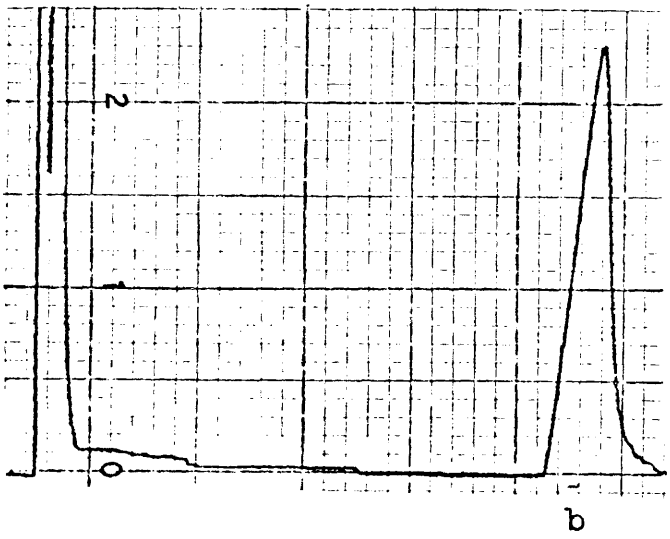
ETHYLATION OF 5-HEXYN-1-OL WITH DIETHYLALUMINUM CHLORIDE

Sample	T(°C)	Time(hr)	Mole % Cp_2TiCl_2	Mole % $AlEt_2Cl$	Yield of Products	Return of 5-hexyn-1-ol
VII-1a	0	4	10	250	not detected	large
VII-1b	0	4	10	250	not detected	large

Figure 36a.
Results: Reaction Group VII
Chromatograms of 5-Hexyn-1-ol
Ethylation Reaction Samples



10% Carbowax



10% XE60

a) 5-hexyn-1-ol
b) 5-hexyn-1-ol

CHAPTER V

DISCUSSION

Characterization of Products

As shown in Figure 5, there are three possible ethylation products for each alkynol studied, assuming an intramolecular addition mechanism. It was concluded from gas chromatographic data that two of those products were formed for the 3-butyn-1-ol (Group I), 4-pentyn-2-ol (Group II) and 4-pentyn-1-ol (Group III) reactions, and that a single product was formed for the 3-pentyn-1-ol (Group IV) and 4-pheynl-3-butyn-1-ol (Group V) reactions. No isolable amount of product was produced for the 2-propyn-1-ol (Group VI) or 5-hexyn-1-ol (Group VII) reactions.

The compounds isolated as products (either singly, or as a mixture, depending upon their separability using available gas chromatographic techniques) were characterized through analysis of their IR and NMR spectra.

All products were expected to exhibit IR absorptions characteristic of compounds with a carbon-carbon double bond, and a hydroxyl group. The olefinic moiety (carbon-carbon double bond) exhibits a strong characteristic absorption at approximately 1650 cm^{-1}. A medium sharp absorption above 3000 cm^{-1} is produced by C-H stretch associated with an unsaturated carbon. The strong, broad, absorption between 3200 cm^{-1} and 3600 cm^{-1} is characteristic of the hydroxyl OH stretch, and the medium to strong absorption between 1080 cm^{-1} and 1300 cm^{-1} is characteristic of the C-O stretch.

The IR spectra of all the isolated products possessed the expected absorptions described above.

Information concerning substitution about the C-C double bond, which is helpful in distinguishing among ethylated products is presented in Figure 36b.

Analysis of the NMR spectra did not yield as many commonalities among products, but the absorptions between 4.6 and 5.9ppm(δ) of the vinylic hydrogen(s) were helpful in distinguishing among the possible substitutions about the olefinic moeity.

Characterization of each reaction group product(s) follows. Structures of the products are shown in Figure 37.

Reaction Group I. Ethylation of 3-Butyn-1-ol with Diethylaluminum Chloride

The IR spectrum of the combined 3-butyn-1-ol ethylation products was ambiguous. The medium absorption at 890cm^{-1} could indicate the presence of the product 3-ethyl-3-buten-1-ol which has a vinylidene structure. The absence of a medium to strong absorption at 1650 - 1700cm^{-1} might indicate the t-3-hexen-1-ol product, but the expected strong absorption between 980 - 960cm^{-1} for this compound is not seen.

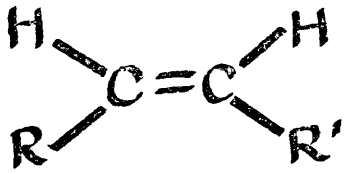
The existence of two products is supported by the NMR spectra. The protons attached to the carbon adjacent to a hydroxyl group would form a triplet between 3.4 and 4.0ppm (δ) if a single product were formed. The methyl protons of a single product would be expected to form a triplet between 0.5 and 1.0ppm(δ). Also the single hydrogen attached to the carbon-carbon double bond would be expected to form either a singlet or a multiplet between 4.6 and 5.9ppm(δ) for a single product.

The NMR spectrum indicates two overlappingtriplets in the methyl region, two overlapping triplets in the CH_2-OH region, and two vinyl hydrogen absorptions, a multiplet at 4.9 - 5.5ppm(δ), and a singlet at 4.6ppm(δ). This then indicates the presence of two products, the multiplet absorption at 4.9 - 5.5 ppm(δ) being assumed from the

Figure 36b.

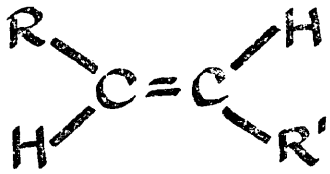
Characteristic Olefinic Infrared Absorptions

<u>cis</u> substituted



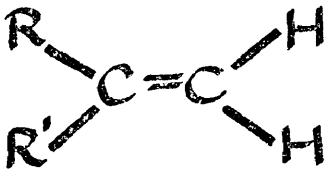
1662-1626 cm^{-1} variable
730-665 cm^{-1} strong

<u>trans</u> substituted



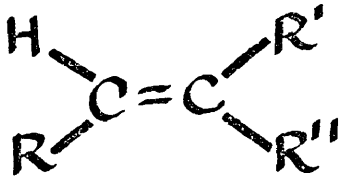
(very weak if R and R' are similar)
1678-1668 cm^{-1} variable
980-960 cm^{-1} strong

vinylidene



1658-1648 cm^{-1} medium
895-889 cm^{-1} strong

trisubstituted

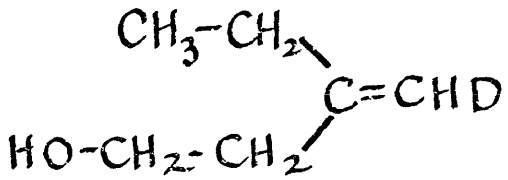


1675-1665 cm^{-1} weak
840-790 cm^{-1} medium

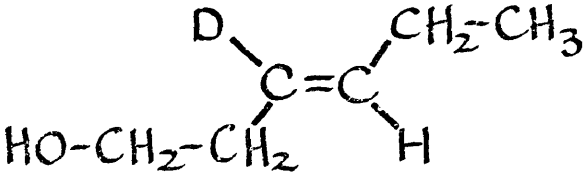
Figure 37.

Structure of Alkynol Ethylation Products

Group I 3-butyn-1-ol ethylation products

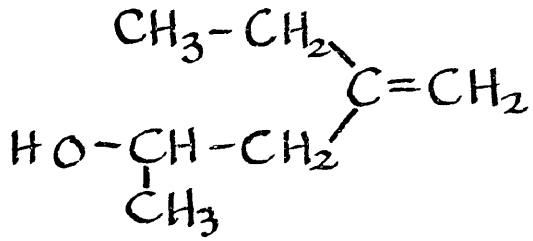


3-ethyl-3-buten-1-ol
(internal addition product)

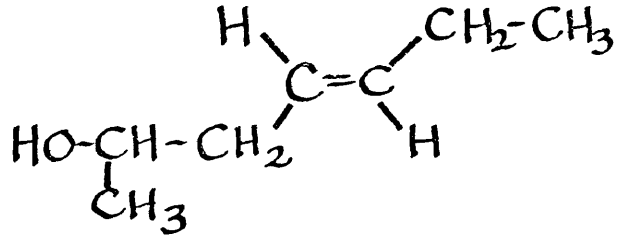


<u>trans</u>-3-hexen-1-ol
(terminal addition product)

Group II 4-pentyn-2-ol ethylation products



4-ethyl-4-penten-2-ol
(internal addition product)

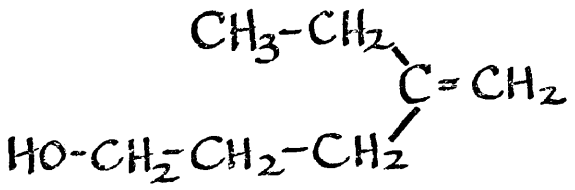


<u>trans</u>-4-hepten-2-ol
(terminal addition product)

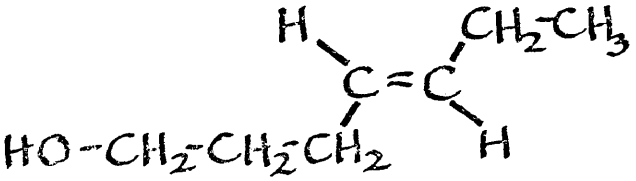
Figure 37.

Continued

Group III 4-pentyn-1-ol ethylation products



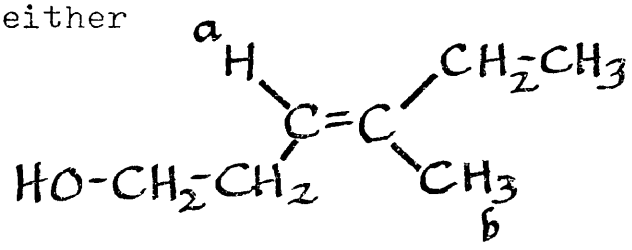
4-ethyl-4-penten-1-ol
(internal addition product)



trans-4-hepten-1-ol
(terminal addition product)

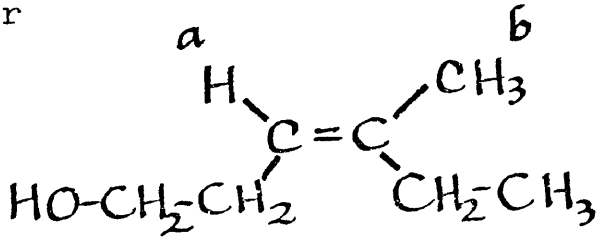
Group IV 3-pentyn-1-ol ethylation product

either



trans-4-methyl-3-hexen-1-ol
(external addition product)

or



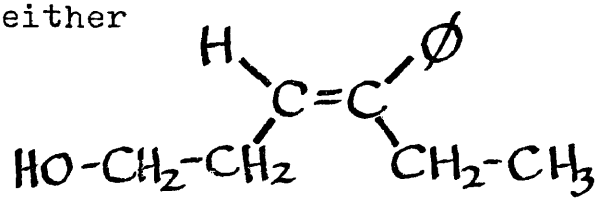
cis-4-methyl-3-hexen-1-ol
(external addition product)

Figure 37.

Continued

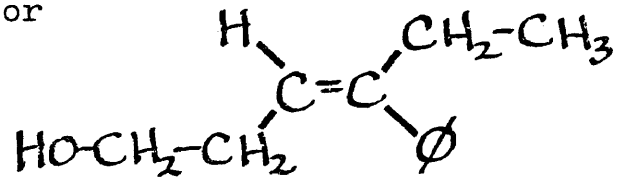
Group V 4-phenyl-3-butyn-1-ol ethylation product

either



<u>cis</u>-4-phenyl-3-hexen-1-ol
(external addition product)

or



<u>trans</u>-4-phenyl-3-hexen-1-ol
(external addition product)

vinyl hydrogen of trans-3-hexen-1-ol. And the singlet absorption at 4.6ppm (δ) from the vinylidene hydrogen of 3-ethyl-3-buten-1-ol.

Integration of the combined vinyl H's area, vs. integration of the CH_2-OH area indicates 97% deuterium incorporation.

The ratio of the 2 vinyl hydrogen peak integrations indicates 85% of the terminal addition product, and 15% of internal addition product.

Reaction Group II. Ethylation of 4-Pentyn-2-ol with Diethylaluminum Chloride

The two products were successfully separated via gas chromatographic techniques. The first product isolated is considered to be the vinylidene product 4-ethyl-4-hepten-2-ol. The characteristic vinylidene IR absorptions at 900cm^{-1} and 1640cm^{-1} as well as the singlet vinyl hydrogen exhibited in the NMR spectrum (4.5ppm(δ)) support this conclusion.

The second product isolated is considered to be the terminal addition product trans-4-hepten-2-ol. The characteristic trans-substituted olefinic IR absorption at 970cm^{-1} as well as the absence of an absorption at 1672 - 1625cm^{-1} support this conclusion. The multiplet at 5.1 - 5.4ppm(δ) in the NMR spectrum is assigned as the vinyl hydrogen absorptions.

Comparison of vinyl hydrogen areas of the combined products indicates 40% terminal addition product and 60% internal addition product.

Reaction Group III. Ethylation of 4-Pentyn-1-ol with Diethylaluminum Chloride

The IR and NMR spectra indicate 2 ethylation products. The presence of 2 methyl triplets (0.6 - 1.1ppm(δ)) and 2 vinyl hydrogen absorptions (a singlet at 4.5ppm(δ) and a multiplet at 5.0 - 5.3ppm(δ)) in the NMR spectrum as

well as the presence of the IR absorptions at 890cm^{-1}, 970cm^{-1} and 1640cm^{-1} indicate both a vinylidene and a trans product.

Comparison of the integrations of the vinyl hydrogen peaks indicates 49% of the internal addition product 4-ethyl-4-penten-2-ol, and 51% of the terminal addition product trans 4-hepten-1-ol.

Reaction Group IV. Ethylation of 3-Pentyn-1-ol with Diethylaluminum Chloride

A single product was isolated. Since the two methyl absorptions in the NMR are a triplet (0.8 - 1.2ppm(δ)) and a singlet (16ppm (δ)), the internal addition product (3-ethyl-3-penten-1-ol) can be eliminated. The internal addition product would be expected to show a methyl triplet, and a methyl doublet.

Differentiation between the two external addition products is difficult since the weak IR absorptions at 840,860 and 1660cm^{-1} and the NMR peaks observed could reasonably belong to either of the products cis or trans - 4-methyl-3-hexen-1-ol. High resolution examination of the methyl singlet might show that is split slightly via coupling with the vinylic hydrogen. Coupling between the vinylid hydrogen and the methyl group in a trans position would produce a different splitting than if the substituents were in a cis position, and the structure might be firmly established.

Reaction Group V. Ethylation of 4-Phenyl-3-Butyn-1-ol with Diethylaluminum Chloride

A single product was isolated. The internal addition product 3-ethyl-4-phenyl-3-buten-1-ol is removed from consideration due to the large splitting (0.5ppm(δ)) of the vinyl hydrogen in the NMR spectrum. The internal addition product would show a singlet, or a minimally coupled multiplet.

Differentiation between the two external addition

products is again difficult since the weak IR absorption at 850 (trisubstituted olefin) and the NMR peaks observed could reasonably belong to either of the products, cis-or trans-4-phenyl-3-hexen-1-ol.

Discussion of Alkynol Ethylations

The investigation of the 3-butyn-1-ol ethylation reaction was carried out with respect to temperature, time, titanium-aluminum-alcohol stoichiometry and solvent. Optimum yield of 91% products was achieved at 0°C after 2 hours utilizing 10 mole % Cp_2TiCl_2 and 250 mole % diethylaluminum chloride with respect to 3-butyn-1-ol, in a methylene chloride solvent system. Considering the results of the recoverability experiment, in which only 85% of the unreacted 6 carbon hexanol was returned, this yield of product may be quantitative. Since yields did not differ greatly on an average between 2, 4, and 6 hours reaction time, a 4 hour duration was utilized in the studies of other alcohols. It should be noted that the benzene solvent system also gave good yields, but for safety reasons, the methylene chloride is preferred. The substitution of dichlorobispentahaptocyclopentadienyl zirconium for the titanium complex did not give substantial yields, even though titanium and zirconium are both in the same group of the periodic table.

Optimization studies of the 4-pentyn-2-ol ethylation reaction with respect to temperature and titanium complex-alkynol stoichiometry, showed that the 0° temperature was optimum, but that a much larger mole % of Cp_2TiCl_2 was required to produce a substantial yield of products.

The remaining alkynols which gave promising yields of product(s) were run utilizing 0° reaction temperature, 4 hours reaction time, 250 mole % diethylaluminum chloride, and approximately 50 mole % dichlorobispentahaptocyclopentadienyl titanium(IV) with respect to the alkynol in methylene chloride.

The 2-propyn-1-ol and 5-hexyn-1-ol did not react to give isolable amounts of products. The remaining alkynols all gave at least 40% yield of product(s).

For the 3-pentyn-1-ol and 4-phenyl-3-butyn-1-ol ethylations a single external addition product was produced. For the 3-butyn-1-ol, 4-pentyn-2-ol and 4-pentyn-1-ol ethylations, both the trans external addition product, and the vinylidene internal addition product were produced.

Details of a reaction mechanism are incomplete, but this data, coupled with that of Tweedy, et al., would suggest that alkylation is accomplished by intramolecular addition of an alkyl-titanium linkage across the triple bond of the titanium bound alkynoxy group.

The fact that 2-propyn-1-ol and 5-hexyn-1-ol do not give significant alkylated product(s) is consistent with an intramolecular addition. Both alkynols are prohibited from forming a chelate ring with titanium through oxygen and the triple bond, 2-propyn-1-ol for steric reasons[10,11,12], and 5-hexyn-1-ol from consideration of entropy, angle strain, and internal eclipsing.[13]

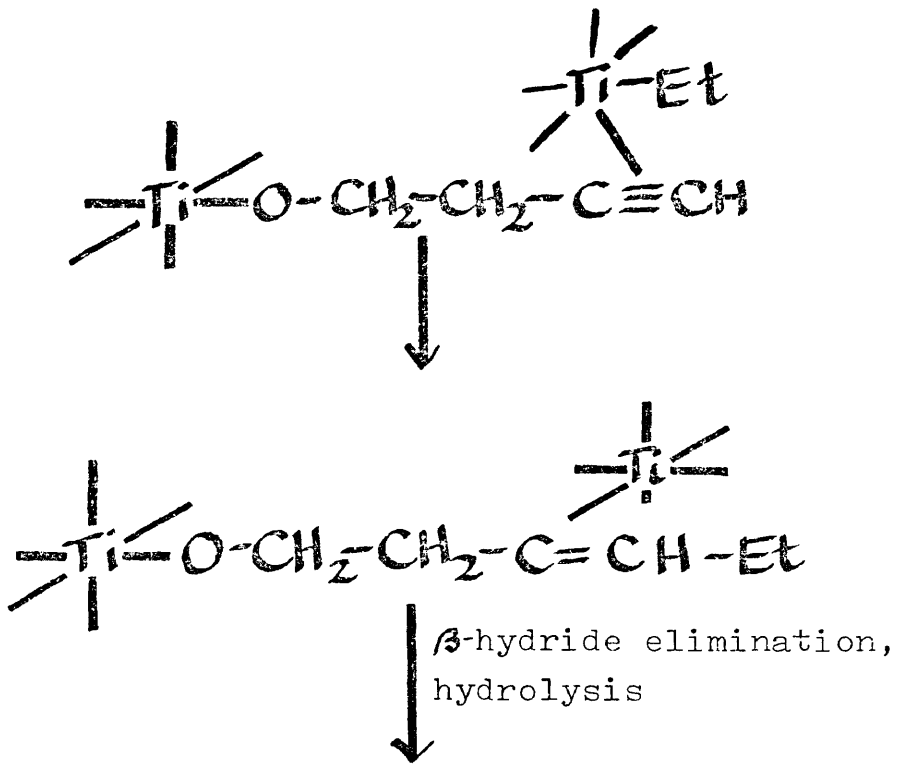
In addition, the fact that no alkylated alkynols are formed supports the intramolecular mechanism. The hydrogens available in an intermolecular mechanism would facilitate a β hydride elimination to the alkylated alkynol products. However, the intramolecular mechanism would lead to an intermediate in which one β hydride is trans to the titanium and the other is endocyclic. (See Figure 38) Both types of β hydrides have been shown experimentally to be difficult to eliminate[14,15]. Therefore, in the 3-butyn-1-ol alkylation, expected products of an intermolecular mechanism would include 3-hexyn-1-ol and an allene (2,3-hexadien-1-ol). Neither of these products was detected.

The existence of trans and vinylidene products would support a cis-addition within the intramolecular mechanism.

Figure 38.

Consideration of Possible β-hydride Eliminations for Intra- vs. Intermolecular Mechanism of 3-butyn-1-ol Alkylation

Intermolecular Mechanism



HO-CH_2-CH_2-C≡C-Et

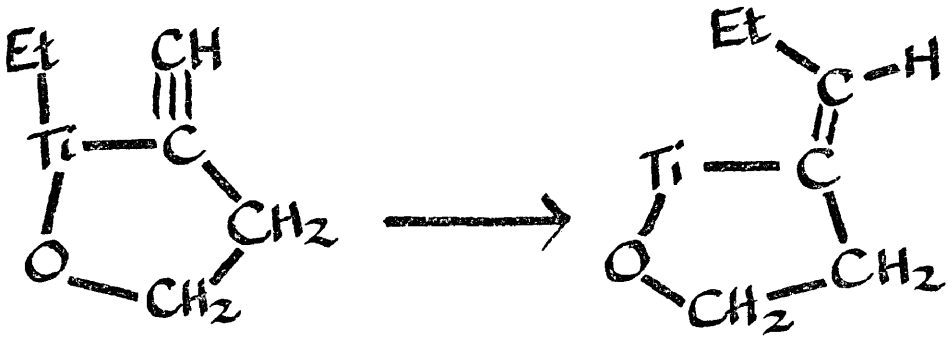
and/or

HO-CH_2CH=C=CH-Et

Figure 38.

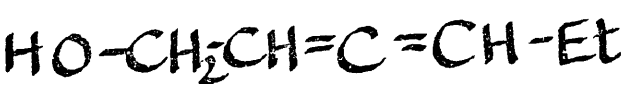
Continued

Intramolecular Mechanism



(no) β-hydride elimination,
hydrolysis

and/or



The single product produced in the 3-pentyn-1-ol and 4-phenyl-3-butyn-1-ol is not explained easily, but the presence of a substituent other than hydrogen on the external acetylenic carbon ($-CH_3$ for 3-pentyn-1-ol, and $-C_6H_5$ for 4-phenyl-3-butyn-1-ol) would seem responsible for this.

The titanium complex did function in a catalytic manner as demonstrated by an average turnover of 8 alkynol molecules for each titanium in the optimized 3-butyn-1-ol ethylation. The required excess of diethylaluminum chloride is deemed necessary to facilitate the bridging interactions and ligand exchange processes which would promote this catalytic function.

Further work relating to titanium assisted alkynol alkylations could more effectively exploit the role of ligands about the titanium molecule as related to the regiospecificity of a reaction. The large fin-like acetyl-acetonato ligand (which projects outward from the titanium atom) present in the system studied by Tweedy, et al. appears to permit only external addition. The plate-like shape of the cyclopentadienyl ligand (which lies in a plane perpendicular to a line drawn from its center to the titanium atom) permits both internal and external addition. "Tuning" of the ligand environment may produce a system which would allow only internal addition, greatly broadening the scope of these titanium assisted alkynol alkylation reactions.

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